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THERMAL DECOMPOSITION AND COMBUSTION OF EXPLOSIVES

By

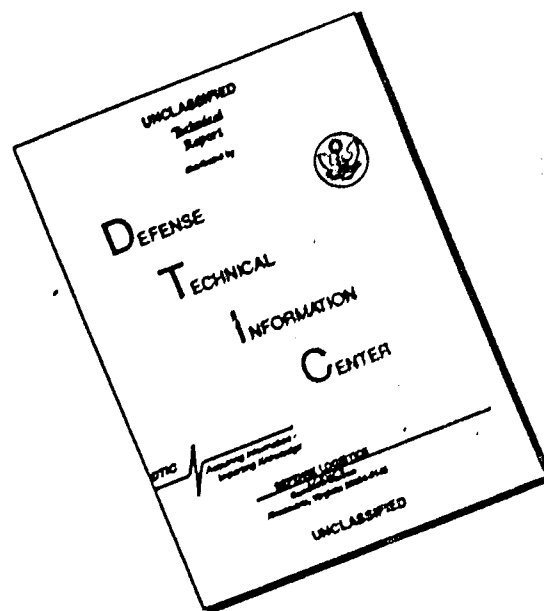
K. K. Andreyev



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EDITED TRANSLATION

THERMAL DECOMPOSITION AND COMBUSTION OF EXPLOSIVES

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Explanation of Foreign Subscripts and Abbreviations

<u>Cyrillic</u>	<u>Translation</u>	<u>Foreign Word</u>	<u>Meaning</u>
кон	con	концентриро-	concentrated
г	g	газ	gas
м	m	материал	material
п	p	предельный	limiting
к	k	критический	critical

CHAPTER 2

SLOW CHEMICAL CONVERSION OF EXPLOSIVES

The combustion of explosives is a self-propagating exothermic reaction. This self-propagation of the reaction occurs as a result of the transmission of heat liberated in the reacting layer adjacent to it into the layer of explosive material not yet taking part in the reaction. The heating of the layer of explosive material causes a chemical reaction to occur, which increases in rate along with the increasing temperature. Since the reaction is exothermic, it is accelerated by heating from the preceding layer and, at a certain stage of its development, becomes itself the main source of heat.

Thus, one of the elements of the combustion process is the chemical conversion occurring at high and increasing temperatures. This conversion occurs also when explosives are ignited at the surface from which combustion begins.

A knowledge of the regularities of slow chemical conversion of explosives is a necessary prerequisite for the construction of a theory of the combustion of explosives and its application to concrete explosive materials. The greatest interest is felt in rapid processes occurring at relatively high temperatures: under the combustion conditions, heating of the layer entering into the reaction occurs comparatively quite rapidly, and the chemical conversion occurs primarily in the area of high temperatures, where its characteristics and the regularities of its occurrence may be quite different than at low temperatures. However, most of the corresponding investigations have been performed in the area of relatively low temperatures since, on the one hand, a quantitative study of the kinetics of the chemical conversion of explosives at high temperatures is more difficult and, on the other hand, in most cases investigations have been performed for a purely practical purpose--the establishment of the chemical stability of the explosive material being studied for purposes of storage. Therefore, it is not always possible to transfer the results of investigations of the low temperature decomposition of explosives directly to the conditions under which their chemical conversions occur during combustion.

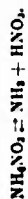
Investigations have been performed at relatively high temperatures only for the establishment of the flash point of explosives under various conditions and

the time dependence of the delay of ignition on temperature. These investigations have yielded considerable interesting material, but their theoretical interpretation has been presented in only a few cases, primarily for gas systems, due to the great complexity of the phenomena involved.

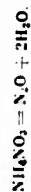
Application of the regularities of the course of a chemical reaction as analyzed by the classical theory of chemical kinetics to the slow thermal conversion of liquid and solid explosives, which occurs at temperatures below their flash point, is difficult due to the complexity of the reactions which occur in this case.

As a rule, thermal conversion of explosives includes not one but several reactions occurring in parallel or in sequence, various reactions predominating depending on the conditions.

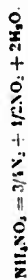
For example, ammonium nitrate is reversibly decomposed to ammonia and nitric acid at about 100°C according to the equation



At about 200°C, the principal reaction is the formation of nitrous oxide and water, according to the equation



At yet higher temperatures, decomposition of ammonium nitrate can be described by the equation



A similar change in the composition of the decomposition products with changing temperature has been established for the thermal decomposition of nitroglycerin and nitrocellulose [7]. The composition of the gaseous products of decomposition (excluding water) produced at various experimental temperatures can be seen from Table 1.

Table 1

Composition of Gaseous Decomposition Products of Nitroglycerin and Nitrocellulose as a Function of Temperature

Decomposition Products	Composition of Decomposition Products, %				
	Nitroglycerin		Nitrocellulose		
	85-90° C	100° C	120° C	130° C	145° C
CO ₂	34	30	30.2	35.7	
CO	6	22	17.4	16.8	
NO	52	37	21.4	29.6	
N ₂ + N ₂ O	8	11	31.0	18.5	
Gas volume, cm ³ /g	—	—	156.5	290	
Total weight loss, %	—	—	48.6	65	

Even such simple compounds as the azides, for example, calcium azide (CaN₆) produced different decomposition products at different temperatures: at low temperatures (100-150°C) a material is produced which corresponds to the empirical formula (CaN)_n, while flash ignition produces the nitride and metal [8].

Furthermore, for many explosives not only are different decomposition products produced at different temperatures, but also the composition of products may vary within a single experiment conducted at constant temperature.

We can see from the data of Sapozhnikov [7] that when nitrocellulose decomposes at a temperature near the flash point, the content of nitrogen compounds in the gaseous products at the beginning of the experiment, expressed in grams, is 6.5 times greater than the content of carbon compounds; at the end of an experiment, the nitrogen content in the gaseous products is only 1.5 times greater than the carbon content.

When liquid nitroesters are decomposed (nitroglycerin, nitroglycol, methyl nitrate) are decomposed in an evacuated and sealed ampule at various temperatures from 70 to 240°C, during the initial stage of decomposition, strong brown coloration of the gas phase was observed as a result of the formation of nitrogen dioxide. Then, the intensity of coloration of the gases decreased, and finally the gases became colorless. Since analysis has shown a considerable content of oxides of nitrogen in the gaseous decay products, it is natural to assume that the decoloration of the gases occurred as a result of oxidation of organic

compounds formed in the initial stages of the decomposition, and possibly even of the initial nitroesters, by the nitrogen dioxide.

No matter what the mechanism, this complication of the course of thermal decomposition of explosives considerably decreases the reliability of conclusions made in a number of investigations which failed to consider the specific features of the processes involved.

Let us analyze investigations on slow thermal decomposition of explosives for their primary representatives and certain generalizations which can be made on the basis of the data available.

I. Nitrates and Nitrites of Polyhydric Alcohols

The full nitric acid esters of the polyhydric alcohols are of the greatest technical significance—glycerin, ethylene glycol, diethylene glycol, biethanol, nitraline, pentaerythrite, cellulose; therefore, their thermal decomposition has been studied in the greatest detail. At moderately high temperatures, the first four nitroesters are in the liquid state, while pentaerythrite tetranitrate melts at 140°C, but can be "liquified" at lower temperatures by dissolving it in a low-melting solvent; nitrocellulose does not go over to the liquid state up to the flash point, but, as a high polymer with highly developed surface, acts in certain respects like the liquid nitroesters. The low molecular nitroesters can be produced in the form of vapors as well.

A change in the bulk state is importantly reflected in the rate of decomposition, in its change with time and influence on the decomposition of certain impurities. Therefore, analysis with experimental data on decomposition of nitroesters will be performed considering their bulk state.

1. Nitroglycerin and Nitroglycol

The kinetics of thermal decomposition of liquid nitroglycerin were first studied by Robertson [9]. At that time the experiments of Ville [10] had shown that decomposition of nitrocellulose in a current of inert gas occurs at constant speed, while it accelerates in the presence of the decomposition products as they accumulate. Therefore Robertson, in order to eliminate the supposed accelerating influence of the gaseous decomposition products, conducted his experiments with nitroglycerin, as did Ville, in a current of inert gas (CO₂). He established that under these conditions almost all of the nitrogen is split off in

the form of NO_2 ; determination of the nitrogen dioxide was performed spectroscopically and was checked by reduction of the oxides of nitrogen over heated copper to nitrogen; the rate of separation of the nitrogen remains constant throughout the entire course of the experiment (4 hours at 120°C , total quantity of nitrogen separated 3x) and depends strongly on the temperature. According to the data produced at various temperatures ($90-120^\circ$), which form a straight line in coordinates $\log (\Delta N_2/\Delta t) - 1/T$, the activation energy can be calculated as $E = 43,700$ cal/mol and the factor before the exponent $B = 10^{18.64} \text{ sec}^{-1}$ in the Arrhenius equation $k = B e^{-E/RT}$.

Objective investigation of the thermal decomposition of nitroglycerin was performed by Roginskiy et. al. [11]. Decomposition was studied with constant volume, and its rate was determined by the increase in pressure of the gaseous decomposition products.

It was established that decomposition occurs differently, depending on the temperature and on the degree of filling of the vessel δ --the ratio of the volume of the nitroglycerin to the volume of the vessel in which it is contained¹.

At high temperatures (150°C) and low δ , the rate of gas formation is proportional to the quantity of undecomposed nitroglycerin. At lower temperatures and higher δ , gas formation first occurred at low rate, then accelerates rapidly.

Roginskiy explained these regularities by the fact that the decomposition of nitroglycerin is autocatalytic in nature, the catalyzing products of decomposition being in the gaseous state at the experimental temperature, and their concentration in the liquid nitroglycerin thus being dependent on the temperature and pressure, which are proportional to δ at a certain stage of decomposition.

Like Robertson, Roginskiy obtained a high temperature rate factor at low degrees of decomposition, corresponding to considerable activation energy. Since the rate constant is also rather high ($2.2 \cdot 10^6 \text{ sec}^{-1}$ at 120°C), this leads to anomalously high values of the factor before the exponent ($10^{20-23.5}$), which change slightly as the temperature is changed.

¹ See p. 131

Later investigations [12-20] were also performed by the manometric method, but using Bordon type glass manometer, which eliminated the defects of the ordinary manometric method (contact of vapors of manometer fluid with explosive and products of its decomposition, possibility of removal by distillation into cold portions of instrument, particularly when experiments are conducted in a vacuum, etc.)

The manometer (Figure 1) is a thin walled glass membrane 1 with a sickle-shaped cross-section, attached to indicator 2. The reaction vessel 3, in which the charge of explosive to be investigated is placed, is connected to the inner space of the membrane. The gases formed when the explosive decomposes press on the walls of the membrane, as a result of which it is bent, and the indicator is deflected from its initial position. Air is forced into tube 4 surrounding the membrane, which is connected to a liquid manometer, until the arrow is returned to the zero position. The pressure of the air forced into tube 4 is red (with an accuracy of 0.5 mm) from the liquid manometer.

Neck 5 is used for the introduction of the explosive material, after which it is sealed off; tube 6, with its narrow section, connects the reaction vessel 3 with a vacuum pump, and is sealed off after the air is evacuated.

Experiments have shown that the decomposition of liquid nitroglycerin occurs clearly in two stages. The onset and development of the second stage is related to the accumulation of volatile decomposition products in the liquid, which depends on δ . With low values of δ , the second stage may not arise to the end of decomposition; on the other hand, with high values of δ it begins quite early. The onset of the second stage may be essentially accelerated by artificial introduction of impurities to the nitroglycerin, consisting of some of the materials formed during decomposition, in particular water. Finally, if decomposition is performed with very low values of δ , when all of the nitroglycerin is in the vapor state, the course of decomposition differs from the decomposition of the liquid material.

In correspondence with this, we will analyze the decomposition of nitroglycerin: a) with moderate δ ; b) with large δ ; c) in the presence of water or other impurities which accelerate like water or delay the development of decomposition and d) with small δ , i. e. in vapors.

At the same time as nitroglycerin, we will analyze data for nitroglycol,

which is similar in many characteristics of decomposition, although this nitro-ester has been much less thoroughly studied.

The decomposition of liquid nitroglycerin with moderate degrees of filling of the vessel was studied between 80 and 165°C. Throughout this entire interval, gas formation occurs at a rate which increases only slightly (in its absolute value) with time. The acceleration is expressed more weakly, the higher the temperature with otherwise equivalent conditions. At 125°C ($\delta = 9.7 \cdot 10^{-4}$), the maximum rate of gas formation exceeded the initial rate by only approximately 1/3. Possibly, even this slight acceleration is not a specific characteristic of the first stage of the reaction, but results from the fact that at the same time, although only to a slight extent (corresponding to the low pressure of the decomposition products) some second stage reaction occurred. Furthermore, apparently, δ influences the first stage in a manner the reverse of its influence on the second stage. Thus, during decomposition of nitroglycerin and nitroglycol, as δ increases in the area of its low values the initial rate of gas formation (Figures 2 and 3) decreases clearly, particularly at high temperatures. For nitroglycerin, the rate maximum also decreases, which can be seen on Figure 2; these influences of δ are observed for the decomposition of PETN as well.



Figure 1. Diagram of glass Bourdon compensation manometer.

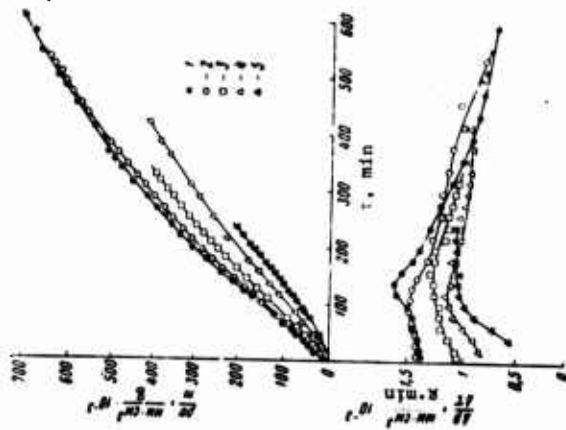


Figure 2. Decomposition of nitroglycerin at 140°C and various moderate m/v ratios (in $\text{g/cm}^3 \cdot 10^{-4}$): 1, 5.0; 2, 5.8; 3, 18.9; 4, 18.6; 5, 47.

The decomposition of liquid nitroglycerin at high degrees of filling of the vessel, during the initial stages, while the pressure of the gaseous products is low, occurs with practically the same low speed as with low δ (Figure 4), slightly increasing ($\sim p^{1/2}$) during the course of decomposition. However, after the pressure reaches a certain critical value, the rate begins to increase much more rapidly ($\sim p^2$) and may even reach quite high values at low temperatures, hundreds and thousands of times greater than the initial values. In this case the gas composition also changes, which can be determined by the sharp increase in their brown coloration (accumulation of NO_2) and the sharp increase in the proportion of gases condensing at room temperature. Svetlov [21] determined the solubility of nitrogen dioxide in nitroglycerin in the temperature interval 20-80° as pressure varied between 100 and 900 mm Hg. The solubility is proportional to pressure with a power of 1.5-2.3, which, apparently, must be explained by the preferential solution of the dimer N_2O_4 . Actually, calculations show that if we relate the N_2O_4 concentration in solution to its concentration in the gas phase, a direct proportionality is seen between them. The solubility constant varies from 0.00170 mm^{-1}

at 20° to 0.00021 mm⁻¹ at 80°C. At the critical pressure (80°), the concentration of N₂O₄ in the nitroglycerin fluctuates between 0.001-0.004%. Comparing these data with the dependence of the rate of the second stage of the reaction on pressure, Svetlov concluded that it is determined by oxidation performed by the nitrogen tetroxide. At 100°C over a considerable interval of δ ($14 \cdot 10^{-4}$ - $440 \cdot 10^{-4}$) the sharp change in the rate of increase of gas formation rate occurs at practically the same pressure (180-200 mm), although the time required to reach it differs by orders of magnitude. In this, whereas the rate of gas formation is somewhat dependent on δ before the critical pressure is reached, decreasing generally as it increases, at pressures over the critical value the rate at a given pressure of decomposition products is practically identical regardless of the value of δ . Only at extremely high δ , i.e. with rapid increase in pressure with time, in other words, with short induction periods, does the value of critical pressure rise; with δ near 1, it is 800-900 mm.

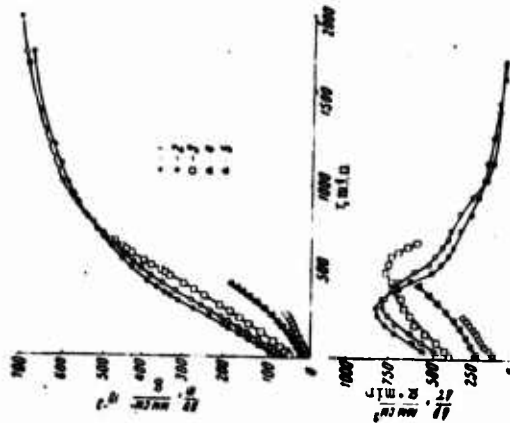


Figure 3. Decomposition of nitroglycerol at 140°C and various moderate m/v ratios (in g/cm³·10⁻⁴): 1, 10.9; 2, 13.5; 3, 18.3; 4, 45.9; 5, 117.2

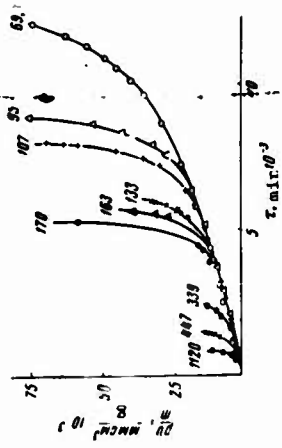


Figure 4. Decomposition of nitroglycerin at 100°C with high m/v ratios. Numbers over curves indicate m/v ratio in g/cm³·10⁻⁴.

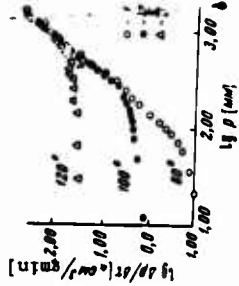


Figure 5. Influence of decomposition product pressure on rate of decomposition of nitroglycerin at 80, 100 and 120°C with moderate m/v ratios (in g/cm³): 1, $543 \cdot 10^{-4}$; 2, $507.2 \cdot 10^{-4}$; 3, $537 \cdot 10^{-4}$.

Thus, the critical pressure depends to a certain extent on the degree of decomposition; in later stages, the gases are somewhat more effective than at the beginning of decomposition. Apparently, this is related to the change in gas composition, in particular as they are enriched with water. The time of onset of the sharp acceleration, naturally, depends on δ decreasing as it increases and where δ is near 1 is about 9 hours; the quantity of gases formed by this time is on the order of 1 cm³/g.

? See p. 131

The critical pressure depends also on the experimental temperature, increasing as it increases (Figure 5). At 80°, it is 60-80 mm, at 120°C 400 - 500 mm. These data relate to $\delta \approx 10^{-2}$; where δ is near 1, the critical pressure at 80° increases to 500 mm; at 60°C it is 250 mm.

This dependence is apparently determined primarily by a change in the solubility of the gaseous decomposition products in liquid nitroglycerin, as well as by changes in the rate constants of the first and second stages. The temperature has practically no influence on the rate of the second stage. More precisely speaking, this influence is apparently so weak that the increase in rate as temperature increases is compensated for by a decrease in concentration of the gaseous products. At low temperatures and high δ , the influence of temperature on the rate of the second stage becomes more noticeable (Figure 6), but as before it remains much weaker ($E = 15$ kcal/mol) than for the first stage.

The dependence of the decomposition rate on temperature in its early stages was calculated for experiments both with small and with moderate δ . In both cases, it is expressed by a straight line in Arrhenius coordinates, although in the first case the dependent is stronger ($E = 43.7$ kcal/mol and $\log B = 18.4 \text{ sec}^{-1}$), than in the second case ($E = 39.3$ kcal/mol and $\log B = 15.4 \text{ sec}^{-1}$). It is interesting that the first set of values is identical to that determined by Robertson when the gaseous decomposition products were removed. This confirms that the decomposition products actually have no accelerating influence on the first stage.

The problem of the reality of the critical pressure is debatable. It is possible [16, 17], that the nature of the curve $W(p)$ observed results from the fact that gas formation is determined by two reactions occurring simultaneously, the rate of one of which is independent of pressure, while the rate of the other is proportional to the square of pressure. The argument in favor of this assumption is the fulfillment of the dependence characteristic for the second stage throughout a considerable portion of the induction period, if we lay out the instantaneous rate of gas formation minus the initial value on the ordinate (Figure 7).

The decomposition of nitroglycerin in the presence of elements which accelerate or delay the process (water, oxygen, nitrogen oxides, soda, chalk). G. O. Novikov [22] determined the solubility of water in nitroglycerine³ in the pressure

³ See p. 131

interval 16-120 mm and the temperature 30-90°C. The solubility constant (ratio of concentration of water and nitroglycerin to equilibrium vapor pressure) decreases with temperature according to the equation

$$\lg K = -9.114 + 1550/T.$$

We present below the contents of water in its saturated solution (in %) at various temperatures:

	20°C	40°C	60°C	80°C	100°C	120°C
	0.26	0.38	0.51	0.66	0.81	0.97

Thus, water is poorly soluble in nitroglycerin; therefore, its content can vary only within relatively narrow limits, which can be achieved by changing the pressure of water vapors over the nitroester.

The nature of the curves $p(t)$ during decomposition of nitroglycerin in the presence of water depends on its relative content; with low quantities of water, it is generally the same as for anhydrous nitroglycerin (Figure 8). The pressure increases first slowly, but more rapidly than for anhydrous nitroglycerin, and the ordinary acceleration of gas formation occurs earlier. Both of these differences are expressed more strongly, the higher the water content.

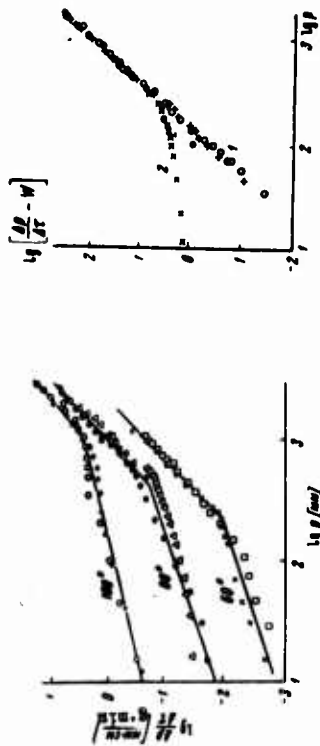


Figure 6. Influence of decomposition product pressure on rate of decomposition of nitroglycerin at 60, 80 and 100°C and degree of filling equal to ~ 1.

Figure 7. Influence of decomposition product pressure on rate of decomposition of nitroglycerin: 1, experiments at 80, 100 and 120°C (initial rate subtracted from instantaneous rate); 2, initial data for experiment at 100°C.

With moderate quantities of water (over 30-50 mm), the change in pressure with time is unique (Figure 9). After establishing the equilibrium pressure, it remains constant for some time, then rapidly and strongly decreases, after which it begins to increase more or less rapidly. The induction period (time before beginning of drop in pressure) fluctuates strongly, but in general has a tendency to increase with increasing quantities of water; an increase in the temperature decreases the length of the induction.

The change in gases which condense at room temperature during the course of decomposition is interesting (Figure 10). It decreases during the stage of pressure decrease and slowly begins to increase with the subsequent increase in pressure. The nature of change with a temporary interruption of decomposition is different before and after the pressure minimum. Gases which do not condense at the temperature of liquid nitrogen appear only during the stage of the rapid acceleration of gas formation.

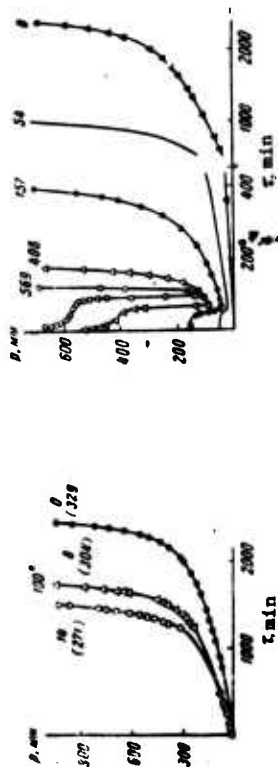


Figure 8. Decomposition of nitroglycerin at 100°C and small quantities of added water. Numbers next to curves indicate equilibrium pressure of water vapor, in parentheses - $\delta \cdot 10^4$.

With higher quantities of water, the nature of the curve $p(t)$ changes once more. At the beginning of the experiments, a slow decrease in pressure is observed, then an equally slow increase. Sharp acceleration occurs considerably later than even during decomposition of dry nitroglycerin. The dual nature of the influence of water (acceleration at low contents, retardation at high contents) is particularly clearly seen in experiments with low δ (Figure 11).

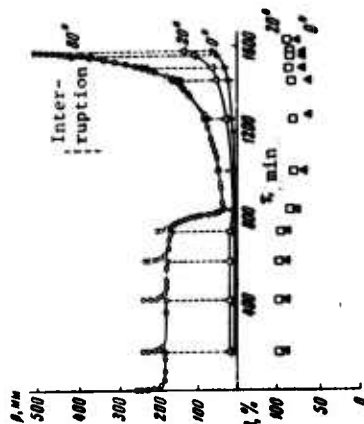


Figure 10. Change in pressure and quantity of gases condensing at 20 and 0°C during course of decomposition of nitroglycerin at 80°C in the presence of water. $p_{H_2O} = 185$ mm Hg; $\delta = 0.0328$.

An increase in δ with this water vapor pressure, representing a decrease in its total content with constant initial content in the nitroglycerin, leads to a decrease in the induction period.

Experiments on the influence of water were also performed at low temperatures with high δ [23]. Under these conditions, the time to the sharp increase is shortened by water considerably less sharply, for example, at 100°C and 0.2% water ($p_{H_2O} = 100$ mm) only by 2.5 times, and at 60 and 40°C, even possibly somewhat less; with a further increase in the water content (0.4%), the induction period continues to be shortened, although more slowly. During the stage of rapid acceleration, the same dependence $w \approx p^2$ is observed, but the proportionality coefficient is somewhat higher than for dry nitroglycerin.

Experiments in which water was added to nitroglycerin which had already been decomposing for a short period of time are quite interesting. The expected rapid onset of pressure decrease was not observed. On the contrary, it occurred if the preliminary decomposition had been performed in the presence of a tiny quantity of water.

In order to explain these unique facts, a determination was performed for the acids formed in the decomposition of nitroglycerin in the presence of water. The acid found was nitric acid, produced as a result of hydrolysis of nitroglycerin, and the quantity of nitric acid is relatively very small. By the

In addition to the catalytic effect on the hydrolysis, the nitric acid formed also has an oxidizing effect. However, at those concentrations at which it influences hydrolysis strongly, the oxidizing effect of the nitric acid, particularly in the presence of the oxides of nitrogen, is still relatively weak. Apparently, when hydrolysis is completed, the concentration of nitric acid is sufficient for considerable acceleration of oxidation, particularly since the concentration of dinitrolycerin, which is more easily oxidized than nitrolycerin, has simultaneously increased.

The decomposition of the mixture of nitrolycerin with dinitrolycerin and nitric acid occurred in a manner quite similar to that observed after the pressure minimum in the decomposition of nitrolycerin in the presence of water. The oxidation of the nitric acid, which develops more rapidly, the more the water and the greater δ , is a self-accelerating process--the nitrogen dioxide is a much more energetic oxidizer than nitric acid alone, and during the oxidation of the dinitrate, obviously, higher oxides of nitrogen are also formed. In addition to this, water is produced, which rapidly hydrolyzes the nitrolycerin in the acid medium, thus supporting additional food for the oxidation, and possibly accelerating the oxidation itself, as can be determined by the sharp increase in the accelerating effect of mixtures of NO and NO₂ on gas formation in the presence of water [24].

These data and considerations allow us to explain the differing nature of the curve of $p(t)$ in the presence of various quantities of water and the absence of any influence of preliminary decomposition of dry nitrolycerin on its subsequent decomposition in the presence of water. If there is little water present, the role of the hydrolytic reaction in comparison to "anhydrous" decomposition is slight, and an acid concentration is rapidly reached at which its oxidizing effect predominates; the rate of oxidation, however, is not great, due to the low concentration of acid. Reduction converts the higher oxides of nitrogen to NO, the influence of which on decomposition is very slight. As a result, decomposition develops like anhydrous decomposition, although more rapidly as a whole since in addition to the anhydrous decomposition oxidation occurs for the nitric acid formed in hydrolysis.

With moderate quantities of water, hydrolysis converts it to nitric acid which, oxidizing the dinitrate preferentially, is reduced, forming NO₂ and water, which accelerate both hydrolysis and oxidation of the organic intermediate products of the decomposition.

-16-



Figure 11. Change in rate of gas formation with time during composition of moist nitrolycerin at 100°C and small δ . Numbers by curves represent equilibrium water vapor pressure; numbers in parentheses show $\delta \cdot 10^4$.

beginning of the decrease in pressure, ~ 0.2% nitric acid had been accumulated, while the decrease in pressure was accompanied by a rapid increase in the quality of HNO₃ and at the pressure minimum almost all the water had been converted to acid, and the nitrolycerin had been converted correspondingly to the dinitrate. The solubility of nitric acid in nitrolycerin is much greater than that of water. This also explains the pressure drop after conversion of water to nitric acid. The greater the quantity of water present, the more acid present at the moment in time when the pressure minimum is observed on the curves; at a given initial pressure of water, the higher δ , the less the acid content.

In the light of these results, the decomposition of nitrolycerin in the presence of water and with no water can be explained as follows. In the presence of water, as a result of ordinary hydrolysis, nitric acid is formed; as the concentration of the acid increases, its catalytic effect in the hydrolysis increases, becoming particularly strong when the acid concentration reached 0.2%. In addition to the catalytic effect, the accumulation of acid doubtless facilitates hydrolysis due to the increased solubility of water in the nitrolycerin--the effective concentration of this participant in hydrolysis is increased. In addition to this, it should be recalled that the rate of hydrolysis catalyzed by nitric acid apparently passes through a maximum at a certain acid content. Obviously, the combination of all these influences leads to the sharp acceleration of hydrolysis observed during the stage of pressure decrease.

-15-

With large quantities of water, it dilutes the acid formed in hydrolysis and therefore makes it impossible for hydrolysis and oxidative reactions to continue development. Therefore, the onset of acceleration can be delayed even in comparison with dry nitroglycerin.

When dry nitroglycerin is decomposed, the nitrogen dioxide formed is apparently primarily reduced and after water is added no acid, or at least no nitric acid, is formed. If, however, decomposition begins in the presence of water, oxidation does not occur at the beginning due to the dilution, and the acid accumulates in quantities sufficient for acceleration of hydrolysis of the water added additionally.

When dry nitroglycerin is decomposed without subsequent introduction of water, the sharp acceleration apparently begins when, as a result of oxidation, sufficient water is accumulated and the oxidizer is formed not only in the process of "dry decomposition", but also by hydrolysis, which occurs more rapidly, since the concentration of acid is high.

The development of oxidative processes depends not only on the content of volatile oxidizers, but also on the quantities and characteristics of materials which can be oxidized. This conclusion has been confirmed both by "aqueous" and by "anhydrous" decomposition of nitroglycerin. Nitroglycerin was decomposed in the presence of water; after the minimum pressure was reached, the volatile products were pumped off, then the experiment was continued. Gas formation was at first quite similar to that produced by undecomposed nitroglycerin, but the acceleration appeared somewhat earlier.

If nitroglycerin prepared in the same manner is decomposed in the presence of water vapors, the course of the curve $p(t)$ and the induction period are approximately the same, but the subsequent acceleration develops more rapidly.

Finally, if dry nitroglycerin is decomposed, and the volatile decomposition products are added to it, the decomposition is developed more slowly than in the corresponding stage of decomposition of moist nitroglycerin; this shows that the undecomposed nitroglycerin is less sensitive to the effects of the decomposition products than partially decomposed nitroglycerin.

⁴ See p. 131.

The conclusions which flow from these experiments are also confirmed by data on the decomposition of dinitroglycerin in the presence of water--oxidation began earlier and continued more intensively than in the decomposition of nitroglycerin.

The formation of intermediate products was established in the "anhydrous" decomposition of nitroglycerin, as well, during the stage of rapid acceleration [25]. Nitroglycerin was decomposed to ~ 10% at 100°C; after extended evacuation of the volatile products, decomposition was continued at this and at lower temperatures (Figure 12). Gas formation occurs at a rate which is little dependent on the temperature ($E = 20$ kcal/mol), but saturating the curve many times (~1000) more rapidly than in the decomposition of fresh nitroglycerin. Only considerably later, at $p > 600$ -700 mm is a sharp acceleration of decomposition noted. The authors noted the similarity of the curves of $p(t)$ produced with the curve of decomposition of nitroglycerin to which a small amount of oxalic acid was added.

If the addition of water as a hydrolysis agent, forming nitric acid, accelerating hydrolysis and oxidizing the organic portion of the molecule, accelerates the decomposition of nitroglycerin, it is natural to expect the same influence upon the addition of nitric acid directly, as well as other acids [26]. Actually, the introduction of a small (0.3%) quantity of nitric acid increases the initial rate of gas formation at 100°C and decreases the time to sharp acceleration, although this effect is considerably greater at equal weight quantities than that of water; apparently the stability of nitroglycerin to oxidation is considerably greater than its stability to hydrolysis.

Keeping in mind the accelerating effect of nitric acid of hydrolysis, it might be expected that it would even more strongly increase the rate of decomposition of moist nitroglycerin. Actually, this acceleration is observed if the content of nitric acid in relationship to the nitroglycerin is 0.1% or more, but is absent at 0.02% acid. This influence appears as a considerable decrease in the induction period, but is not reflected in the subsequent acceleration. This acceleration increases only with considerably greater acid contents, i.e. 1.5%. A similar influence on the induction period is shown by perchloroacetic acid. The influence of oxalic acid is more complex, since it is not only an acid, but a reducing agent as well. At small contents, an increase in the induction period is noted, while at larger contents the acceleration of gas formation

occurs more rapidly than for pure nitroglycerin. However, the form of the curve of $p(t)$ is essentially different.

The onset of accelerating and decomposition of nitroglycerin is made earlier also by the oxides of nitrogen—weakly by nitrogen oxide, more strongly by nitrogen dioxide and even more strongly by the two together [24]. Nitrogen oxide has no influence on the induction period in the presence of water, but eliminates the pressure drop, probably as a result of reduction of nitric acid to nitrous acid, which is assumed less soluble in nitroglycerin, like the oxides of nitrogen, but oxidizes it more energetically. Gas formation is particularly strongly accelerated if water, nitrogen oxide and nitrogen dioxide are all present; the induction period disappears in this case and the time required to reach a certain pressure is decreased by more than 100 times.

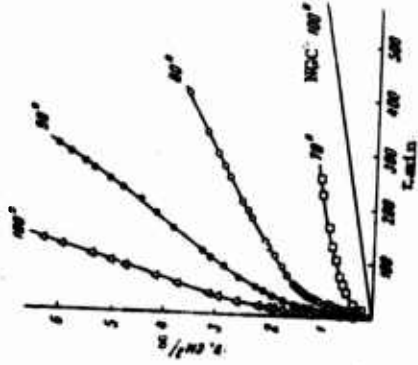


Figure 12. Decomposition of nitroglycerin preliminarily decomposed and evacuated at $\delta = 0.03-0.04$.

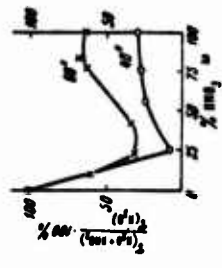


Figure 13. Influence of composition of acid added on induction period during decomposition of nitroglycerin.

These experiments on the influence of acids were conducted at moderate δ and at 100°C. At high δ [23], the influence of nitric acid is relatively weaker. Thus, at 100°C with δ equal to ~ 1 , the addition of 0.2% HNO_3 decreases the time to rapid acceleration by 1.5 times less than the same quantity of water. At lower temperatures, the effect of nitric acid is greater and stronger than that of water. For example, at 40°C acceleration of decomposition with 0.17% HNO_3

occurred four times earlier than in the presence of water. Apparently, the rate of oxidation is less strongly dependent on temperature than the rate of hydrolysis; also, at low temperatures the rate of "anhydrous" decomposition decreases so strongly that it practically ceases to play a role as a source of acid.

Also, the influence of the concentration of aqueous nitric acid, added in quantities of 0.2% during the induction period of 40 and 60°C was studied (Figure 13). 25% acid has the strongest influence.

If nitric acid has a strong role to play in the development of the decomposition of nitroglycerin in the presence of water, acting as a hydrolysis catalyst and oxidizer, its neutralization should slow down the process. Soda, introduced in small quantities (0.07%) to anhydrous nitroglycerin, practically does not change the course of its decomposition at 100°C. This should be explained by the fact that the soda does not influence the primary processes of decomposition, while in the stage of sharp acceleration the quantity of acid is incomparably greater than the quantity of soda added. On the other hand, in the presence of water, soda significantly increases the induction period (quantity of acid by beginning of pressure drop is commensurate with quantity of soda). When large quantities of soda are used (introduced not to the liquid, but to the side arm of the reaction vessel), acceleration of decomposition did not occur over a period of 30 hours at 100°C, whereas without the soda it begins after a few hours. Chalk has a similar effect. If so much dilute nitric acid is added that a portion of it is not dissolved in the nitroglycerin, the induction period can increase strongly.

According to data produced in experiments with large δ , the extrapolation induction period was calculated at 20°C with δ near 1 [18]. For anhydrous and neutral nitroglycerin, it is 17 years, for nitroglycerin containing 0.2% water it is 10 years, for anhydrous nitric acid it is 1.4 years, for dilute nitric acid it is 3 months.

2. PENTAERYTHRYTETRA-NITRATE (PETN) $[\text{C}(\text{CH}_2\text{ONO}_2)_4]$

The slow decomposition of PETN has attracted the attention of investigators for three reasons. On the one hand, PETN has been used in ammunition designed for long term storage, as a solid explosive with high explosion heat. On the

other hand, the resistance of PETN is considerably higher than other nitroesters with similar explosion energy. Thirdly, the addition of such stable explosives as trotyl or even certain nonexplosive materials to PETN has been found in tests using ordinary samples to decrease its stability [27-30].

Investigations have shown [31, 32] that these latter two specifics are related to the fact that PETN was tested at temperatures at which it is in the solid state. When melted or dissolved into the liquid state, PETN decomposes tens of times more rapidly⁵ and becomes similar in its rate and character of decomposition to nitroglycerin and nitroglycol. During the course of decomposition of solid PETN, condensed intermediate products are formed which are soluble in PETN and decreased its melting point. This leads to the fact that an ever greater portion of the solid PETN is converted to the liquid state during the course of decomposition, due to which the total rate of decomposition increases in addition to the increase observed during the decomposition of solid PETN. This explains the increase in the rate of decomposition of PETN when chemically stable impurities which dissolve PETN are added to it. At temperatures below the eutectic point, this influence should not appear.

The dependence of the rate of decomposition on temperature does not fit the Arrhenius equation for solid PETN, possibly as a result of changes in the portion of the PETN in the liquid state at various temperatures due to impurities or condensed decomposition products, which decrease the melting point. Using the points for lower temperatures, $E = 51.5$ kcal/mol. Water or oxygen accelerate the decomposition of solid PETN; this acceleration appears particularly strongly when they are both present.

The thermal decomposition of PETN in the liquid state was studied by A. Robertson [33] at relatively high temperatures (160-225°C) with small charges (1 mg and slightly higher) in order to provide rapid heating and reduce self-heating to a minimum. The PETN was placed in a glass trap in the upper portion of a test tube, the lower portion of which was submerged in a bath. As the trap was rotated, the PETN fell into the test tube. The course of the decomposition was characterized by the increase in pressure. Air or nitrogen (under pressures of 5, 10 and 76 cm) were contained in the test tube, since in a vacuum PETN evaporates rapidly and condenses only in cold portions of the test tube. The

⁵ See p.131

presence of these gases and their pressures have no influence on the rate of decomposition.

The pressure-time curves in the interval 161-233°C show an almost constant rate throughout approximately the first half of the decomposition period, after which the rate decreases in correspondence with the first order reaction equation.

The rate constant for the first stages of decomposition was determined by the slope of the initial straight sector of the curve and the total increase in pressure throughout the experiment

$$k = 10^{11.8} \exp(-47000/RT).$$

In 5% solutions of PETN in dicyclohexylphthalate at 171-238°C, the course of the pressure-time curves in general is the same as for the melted substance. The values of rate constants at moderate temperatures (171°C) are quite similar for the melted substance and for the solution ($4.8 \cdot 10^{-4}$ and $5.0 \cdot 10^{-4}$ sec⁻¹ respectively); at elevated temperatures (i.e., at 238°C) they differ essentially, amounting to 0.49 sec⁻¹ for the melted substance and 0.17 sec⁻¹ for the solution. For the solution

$$k = 10^{11.1} \exp(-39500/RT).$$

Thus, according to Robertson the kinetic coefficients (E and B) of the decomposition of PETN in the melted state are considerably higher than in the solution. Most probably, all of this is explained by the fact that in the case of the melted state as the temperature is increased, an ever greater portion of PETN is in the vapor state, in which the rate of decomposition is higher than in the liquid. Correspondingly, the temperature rate coefficient is increased, as well as E and B.

In another investigation [31, 32], the decomposition of liquid PETN was studied at lower temperatures by measuring the pressure of the gaseous products using a Bourdon type manometer. In the melted state (145-171°C) and in a solution in trotyl (100-145°C) with small δ , the PETN is decomposed in a manner similar to nitroglycerin (Figure 14) but considerably (by a factor of two at 145°C) more slowly. The absolute rate increases to ~30% melts and at its maximum is

2.5 times higher than the initial value. The pressure-time curves can be well matched by changing the time scale, giving $E = 39$ kcal/mol and $\log B = 15.6 \text{ sec}^{-1}$; the rate constant at 160°C is equal to $6.86 \cdot 10^{-5} \text{ sec}^{-1}$.

Experiments in solutions have shown that the solvent does not increase the rate of decomposition, but rather slightly decreases it, particularly in dilute solutions; the rate is also independent of the PETN concentration, that is decomposition is a first order reaction.

With high δ , like for nitroglycerin, the W-p function can be represented in logarithmic coordinates in the form of two straight lines, on which in the sector of sharp acceleration the rate (at 100°C) is proportional to the square of pressure; with very high δ , the rate in both sectors is somewhat less than with moderate δ . According to the initial rates of gas formation $E = 40.1$ kcal/mol and $\log B = 15.8 \text{ sec}^{-1}$, which is very near the values produced for the melt.

As in the case of nitroglycerin, water greatly decreases the time to onset of rapid acceleration during the decomposition of PETN (in a trotyl solution). The oxygen does not influence the rate of gas formation in the initial stage of PETN decomposition at 145°C , but decreases the time to sharp acceleration.

In the work of Robertson [33], the composition of the gaseous products of PETN decomposition were determined. After two minutes heating of PETN at 210° , the decomposition products, in addition to formaldehyde and water, contained the following gases (in moles per mole of PETN): $\text{NO}_2 - 0.51$; $\text{NO} - 2.11$; $\text{N}_2\text{O} - 0.42$; $\text{N}_2 - 0.07$; $\text{H}_2 - 0.09$; $\text{CO} - 0.93$; $\text{CO}_2 - 0.28$. When heating is continued, the nitrogen dioxide disappears as a result of secondary reactions, while the quantity of carbon monoxide and dioxide increases.

In order to determine the quantity of nitrogen dioxide first formed, decomposition was performed in a special device in a current of nitrogen. This method produced 1.1 moles of NO_2 per mole of PETN with complete decomposition at 190°C . The remaining nitrogen was produced primarily in the form of nitric and nitrous oxides, as in static experiments. The flow through method also confirmed the formation of formaldehyde during the decomposition. Robertson assumes that the primary stage in the decomposition of PETN is direct splitting of the NO_2 molecule, which is followed either by splitting of the CH_2O in the form of formaldehyde or oxidation of this segment by the neighboring NO_2 group. In this latter case, the fragment ONO is formed, from which nitric oxide can split off directly.

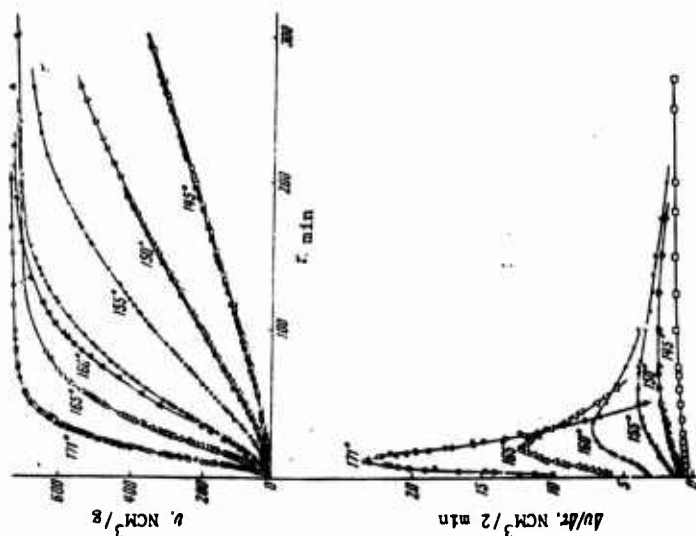


Figure 14. Influence of temperature on decomposition of PETN with small δ .

3. Diethylene glycol dinitrate ($\text{O}_2\text{NOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{ONO}_2$)

The most important specific feature of the thermal decomposition of the nitroesters outlined above (nitroglycerin, nitroglycerol, PETN) is the two-staged nature of the decomposition, in which the second stage is developed under the influence of acids formed during decomposition and accelerating hydrolysis of the nitroester by water, which is a product of the decomposition or present as an impurity. In order for the hydrolysis to occur rapidly, the accumulation of a considerable quantity of nitric acid is necessary. However, nitric acid and the higher oxides of nitrogen, from which can be formed, are energetic oxidizers.

Therefore, if the nitroester itself or its intermediate products are fully reduced by the nitric acid, the acceleration of hydrolysis by the acid, and consequently the second stage of decomposition, will not occur. Examples of such nitroesters include diethylene glycol dinitrate and dina, studied by Svetlov et al [34-36], as well as nitrocellulose.

The decomposition of diethylene glycol dinitrate was studied in the interval 60-150°C over a considerable range of k (0.0013-0.95). The initial rate decreases, as for other nitroesters, as t is increased and increases with temperature: $k = 10^{16.5} \exp(-42500/RT)$. In its absolute value, the rate at 100°C is approximately five times less than that of nitroglycerin, and is quite similar to the rate of decomposition of nitroglycol and nitrocellulose. In contrast to nitroglycerin, the dependence of the rate on temperature does not change throughout the entire interval studied. Due to this, at low temperatures, for example 50°C, the rate of decomposition of diethylene glycol dinitrate is considerable (20-30 times) less than that of nitroglycerin.

Gas formation occurs with a slow and practically constant acceleration--the rate at its maximum is only 3-4 times greater than the initial rate.

We know that the onset of sharp acceleration is facilitated by a low temperature and high degree of filling of the vessel. However, for diethylene glycol dinitrate, as t is increased to 0.95 and the temperature is decreased to 80-60°C, the transition of decomposition to the second stage was not observed. This agrees with the absence of the influence of the water on the course and rate of decomposition. Apparently, the rate of hydrolysis is low in comparison to the rate of anhydrous reactions.

The slight increase in rate observed is probably a result of the course of successive reactions including bonding, and reduction of NO_2 ; this is indicated in particular by the change in gas composition occurring in the early stages of decomposition--the share of gases condensing at room temperature is sharply decreased. The decomposition products under various conditions did not contain nitrogen dioxide in measurable quantities ($> 1 \text{ mm}$). This does not mean that nitrogen dioxide is not formed in the first stage of decomposition, but rather that it rapidly disappears, forming condensed compounds or being reduced by interaction with molecular fragments; experiments have shown that nitrogen dioxide added to diethylene glycol dinitrate disappears.

The bonding of nitrogen dioxide occurs independently of the decomposition of the nitrate, since on the one hand it is observed for diethylene glycol itself and, on the other hand, occurs for the nitrate at a rate considerably greater than the rate of decomposition, particularly at low temperatures (i.e., 50°C). In connection with this, at first we observe a slight decrease in pressure, while subsequently it increases considerably more rapidly than without this impurity. The lower the temperature, the greater the increase in the rate of decomposition resulting from nitrogen dioxide.

A decrease in pressure is observed in the decomposition of diethylene glycol dinitrate in the presence of nitric oxides; this increase in rate occurs somewhat more rapidly than if nitric oxide is absent. Oxygen influences the course of the decomposition in the same way as nitrogen dioxide. At first, a decrease in pressure is observed, then it increases with a rate which may be dozens of times higher than the rate of gas formation in the decomposition of nitrate without additives if there is a great deal of oxygen present. However, the acceleration of gas formation with time is not observed. During decomposition in the presence of oxygen, formation of considerable quantities of NO_2 is noted. The role of oxygen is not simply the formation of NO_2 , which is indicated by bonding of oxygen at the beginning of the experiment, which is observed not only for the nitrate but for the diethylene glycol itself.

Concentrated nitric acid, after a short induction period, leads to rapid decomposition which, however, occurs at a rate decreasing with time. Diluted nitric acid causes a pressure drop at the beginning of the experiment and a more rapid acceleration of its growth in the later stages, apparently as a result of hydrolysis and subsequent oxidation. The acceleration of the decomposition of diethylene glycol dinitrate is observed in the presence of oxalic acid as well.

One essential difference in the decomposition of diethylene glycol dinitrate with these impurities and without them is that a considerable increase in rate with time is not observed, although the impurities may cause the rate to exceed the rate of decomposition of the pure material by dozens of times. The primary factor in the autostabilization of decomposition of diethylene glycol dinitrate is the high rate of reduction of the higher oxides of nitrogen which can form with water to lower oxides, which cannot do this. As a result, conditions are not formed for rapid hydrolysis, which would create a material capable of rapid and accelerating oxidation-reduction reactions.

4. Dina [Dinitroxyethylnitramine, $\text{NNO}_2(\text{CH}_2\text{CH}_2\text{ONO})_2$]

Svetlov and Lur'ye [36] established that at relatively high temperatures and low values of δ , dina decomposes qualitatively and quantitatively similarly, according to the nature of the curves of $p(t)$, to diethylene glycol dinitrate. The relative rate of gas formation at low δ decreases with time (Figure 15), while at high values its rate considerably increases. As the experimental temperature decreases and δ increases, the increase in the rate during the initial stage of decomposition is reinforced (at 60°C it increases by 250 times in comparison with its initial value) and the degree of decomposition at which the rate maximum is reached decreases (Figure 16). In this case after the maximum, however, at particularly low temperatures, the rate remains constant for a considerable time, while at high temperatures it increases slightly. Another difference is the absence of nitrogen dioxide in the decomposition products of both stages, as well as the relatively low content of gases condensing at room temperature, particularly at low decomposition temperatures (3-62). Obviously, no significant quantities of water accumulate during decomposition.

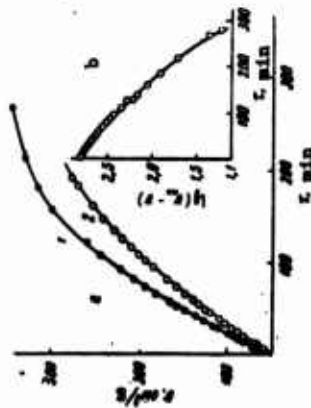


Figure 15. Decomposition of dina at 160°C and low δ : a, 1, 0.0005; b, 0.002; b, least of first order decomposition of dina at $\delta = 0.0005$.



Figure 16. Change in rate of gas formation of decomposition of dina as a function of quantity of decomposition products liberated at $\delta = 0.3-0.5$ and various temperatures.

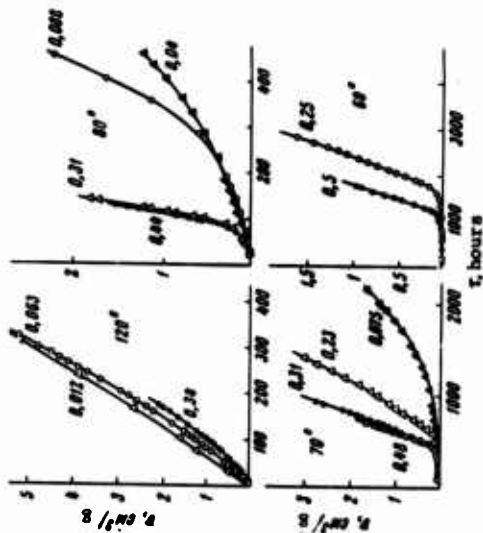


Figure 17. Thermal decomposition of dina at various temperatures and various degrees of filling of vessel (numbers by curves). At 120°C, time in minutes.

The overall picture of the decomposition (Figure 17) indicates its complex, two-staged nature, which appears particularly sharply at low temperatures, when the differences between the rates of the two stages become greater and a considerable increase in the rate of gas formation is seen, resulting apparently from an accumulation of the intermediate product. The influence of δ on the course of the process (Figure 17) indicates the participation of gaseous products in it. The activation energy at elevated temperatures is about 42 kcal/mol ($\log B = 17$). The similarity of this to the activation energy for the decomposition of alcohol nitrates indicates that in the decomposition of dina the primary process is splitting off of the nitroxy nitro group⁶.

The decomposition of dina was also studied in the presence of water vapors. The initial sector of the curve of $p(t)$ in the presence of H_2O is similar to the figures observed for nitroglycerin (Figure 18). The time to onset of acceleration of decay in the presence of water is sharply reduced (by 6-8 times). However, the acceleration observed after the pressure drop, particularly with low water contents, is reduced, which is apparently a result of the decrease in concentration of nitrogen dioxide, established by special experiments; this decrease

⁶ See p. 131

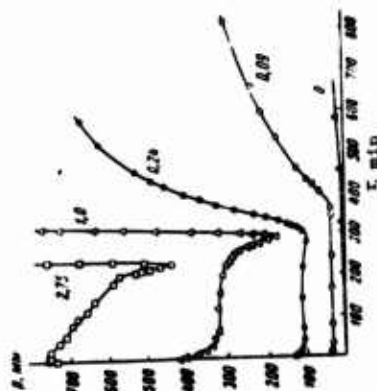


Figure 18. Influence of water on thermal decomposition of dina at 100°C and $\lambda = 0.03$. Numbers by curves indicate water content in relationship to quantity of dina (in %).

results from the rapid entry of NO_2 into the reaction, as was observed in the decomposition of dina in the absence of water. Nitric acid accelerates the decomposition if we exclude the initial sector in a manner similar to water.

5. Nitrocellulose

Nitrocellulose is a high molecular compound which differs essentially from the low molecular nitroesters in its inability to melt, as a result of which it is decomposed at all temperatures in the solid state. In addition to this, nitrocellulose has a physically complex structure, usually a highly developed surface and is generally not a chemically homogeneous material. Finally, when nitrocellulose is produced various impurities are produced which are frequently unstable and difficult to remove. All of these factors briefly complicate the course of decomposition.

Investigations have shown [10, 37-39] that the rate of gas formation and its change with time depend strongly on whether the gaseous decomposition products remain in contact with the nitrocellulose or are removed. In the first case, decomposition occurs with considerable acceleration, while in the second case it is essentially less--the absolute rate of gas formation does not increase with time, but remains constant over a considerable portion of the conversion. Ville separated the gaseous decomposition products by passing a current of inert gas (CO_2) through the decomposing nitrocellulose and determined in the gas the content

of nitrogen as N_2 , the volume of which was used as a measure of the rate of decomposition (Figure 19). The absence of any essential growth in the rate of decomposition of nitrocellulose was also observed when it was decomposed in solutions. Thermal decomposition of nitrocellulose (11.85% nitrogen) was studied for dilute (1%) solutions in inert solvents (1-chloro-2,4-dinitrobenzene, benzophenol, 1-nitronaphthalene) at 165-200°C [40]. The process occurs with the formation of 5 moles of gases per mole of nitrocellulose and is a first order reaction, although deviations from its ordinary course are sometimes observed. For example, over the course of the first third of the reaction, the rate of gas formation in the chlorodinitrobenzene solution decreases relatively slowly and the rate constant increases by approximately 25%; over the course of the last fourth of the decomposition, on the other hand, the constant decreases by almost 60% in comparison with its value in the intermediate stage, and this latter figure is approximately identical in different solvents. The rate constant $k = 10^{18.0} \exp(43,000/\text{RT})$. The mean deviation of experimental values of the constant from calculated values using this equation does not exceed 7%.

Robertson and Nipper [41] determined the spectroscopic content of nitrogen dioxide in the decomposition products in a current of inert gas at 135°C and showed that 40-50% of the nitrogen is contained as NO_2 ; during decomposition for four hours without evacuation of gases, the share of nitrogen in the form of NO_2 was only 25%; the content of nitrogen dioxide also decreases if the inert gas current is slowed down. All of this indicates the comparatively high rate of oxidation-reduction reactions involving this gas. During the course of decomposition, the NO_2/N ratio in the products decreased in one experiment from 54 to 8% by the sixtieth hour, although the absolute rate of nitrogen separation remained constant. This indicates a change in the specific gravity of the individual reactions during the course of decomposition and, possibly, an increase in the role of secondary processes.

If we assume that the decomposition of nitrocellulose includes the primary reaction, the rate of which does not depend on the presence of decomposition products, plus secondary reactions, which do depend on this factor, constancy of the absolute rate, that is the considerable increase in absolute rate during experiments in the current of inert gas, might be related to the incomplete separation of gaseous decomposition products. In this case, with more complete separation, for example by evacuation, a decrease in absolute velocity with time, characteristic for a reaction without self-acceleration, could be produced.

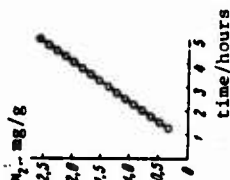


Figure 19. Course of decomposition of nitrocellulose in a current of inert gas at 135°C

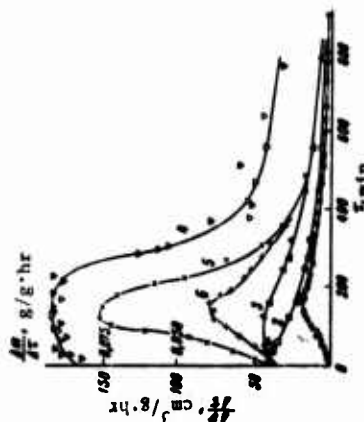


Figure 20. Curves of change in rates with time during decomposition of nitrocellulose (160°C). 1, gases difficult to condense; 2, gases which condense easily; 3, some of difficult and easy condensing gases; 4, weight loss; 5, gas formation without gas evacuation (at 160°C $m/v = 15.8 \cdot 10^{-4}$ g/cm³); 6, gas formation at quasiconstant pressure.

For this purpose, decomposition was performed [42, 44] with the gaseous products evacuated by a diffusion pump, so that the pressure did not exceed 10^{-3} mm. The gases pumped away were passed through one of two parallel, alternately connected traps, cooled with liquid nitrogen. Measurement of the pressure after heating of the trap to room temperature allowed the volume of gases condensed, which had been separated over a defined time interval, to be determined. Short term disconnection of pump and measurement of the pressure increase in

the system (not exceeding 10^{-2} mm) was used to calculate the rate of formation of the gases difficult to condense. A quartz spring balance was used to measure weight loss in the nitrocellulose. The curves of these three rates are shown for three temperatures (160, 150 and 145°C) on Figures 20-22. Separation of the condensing gases at 160°C is retarded. The mean molecular weight of gases, calculated by weight loss of the nitrocellulose, is near 46 at the beginning of the decomposition, that is, near the molecular weight of NO_2 . Since at the beginning of decomposition the share of condensing gases is about 96%, these data indicate that the first stage in decomposition of nitrocellulose is separation of NO_2 . The rate of formation of the gases difficult to condense increases significantly with time; the total quantity, if we extrapolate to $t = 0$, amounts to 120 cm³/g. The share of gases difficult to condense by the end of the experiment amounts to about one-third of the total gas volume. The total weight of gas separation remains approximately constant for some time, then decreases. The curve of the rate of weight loss is similar in nature, although its downward trend occurs more rapidly, which is apparently related to a decrease in the mean molecular weight of the gases.

As the temperature is decreased, the nature of the curves changes somewhat. The rate of separation of condensing gases decreases with time at first considerably slower, and this decrease does not compensate for the increase in the rate of separation of the gases difficult to condense; as a result, the total gas separation increased markedly with time. The acceleration on the curve of rate of weight loss is even more significant. The volume of gases decreases slightly, as does the share of gases difficult to condense.

At 135°C, decomposition was continued for only 13 hours, i.e. for the initial sector (final weight loss 4%); the only sharp increase is in the curve for gases difficult to condense; for condensing gases and weight loss, the rates remain practically constant.

The difference in the curves of $W(t)$ indicates that when nitrocellulose decomposes, at least two successive reactions occur.

According to the nature of the curves, the formation of condensing gases, the rate of which is greatest at the initial moment, should be considered a result of the primary processes, while the formation of the gases difficult to condense is a result of the secondary processes.

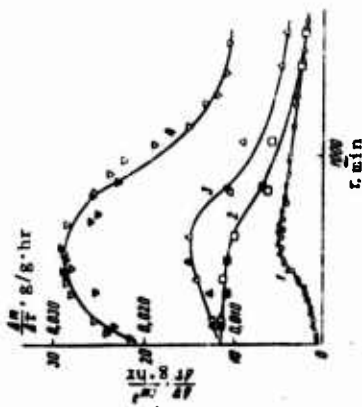


Figure 21. Curve of change in rate with time in decomposition of nitrocellulose (150°C temperature). Symbols same as on Figure 20.

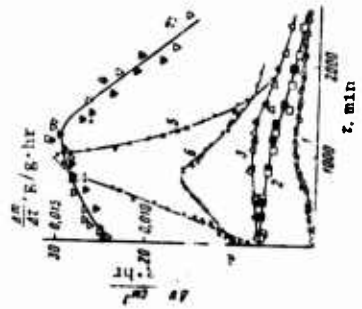


Figure 22. Curve of change in rate with time in decomposition of nitrocellulose (145°C, $m/v = 13.9 \cdot 10^{-4}$ g/cm³). Symbols same as on Figure 20.

The formation of condensing gases cannot be looked upon as a simple monomolecular reaction. Whereas at 160°C the rate of decomposition decreases continually with time approximately according to the rule of a first order reaction, at lower temperatures (150 and 145°C) the decrease in rate occurs at first quite slowly, over the course of a considerable time interval, it remains practically constant. Obviously, this process is complex and possibly occurs through the formation of an intermediate compound, also producing condensing gases upon decomposition. Accumulation of this compound to a certain quastable concentration might give a form to the curve of $W(t)$ as observed in the experiment.

The formation of gases difficult to condense is also apparently related to the accumulation of a certain intermediate product, particularly since the maximum of the curves of rates of weight loss and formation of products difficult to condense are similar in their time of onset. This relationship may be direct, i.e. the products difficult to condense may form (along with the condensing products) in the decomposition of an intermediate product. The relationship may also be indirect if the intermediate product is quite reactive, i.e. to NO_2 and, interacting with it, converts it to the gases difficult to condense; at 150 and 145°C, the rate of formation of condensing gases decreases after the maximum considerably more rapidly than the rate of formation of gases difficult to condense.

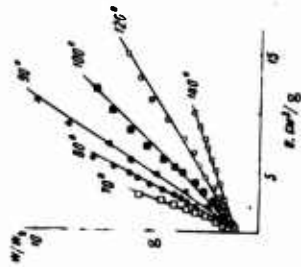


Figure 23. Influence of temperature on acceleration of decomposition of nitrocellulose.

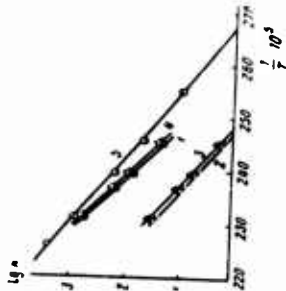


Figure 24. Rate constants as functions of temperature. 1, formation of gases difficult to condense; 2, formation of condensing gases; 3, total gas formation; 4, weight loss; 5, gas formation without evacuation of gases. Constants entered on graph in arbitrary units.

When nitrocellulose decomposes without drawing off its gaseous products or when they are partially drawn off (quasiconstant pressure 10 mm Hg), the initial rate is the same as in a vacuum. The acceleration of gas formation is considerably greater, particularly at low temperatures and high values of m/v . At 160°C, the ratio of rates of gas formation in the presence of decomposition products and with quasiconstant pressure (Figure 20) is 1.9 at the maximum, while at 145°C it is 2.1 (corresponding pressures in experiments without gas evacuation amounted to about 400 mm); at lower temperatures, apparently, it increases even more, as would be expected due to the lower temperature dependence of the processes being analyzed.

The increase in acceleration of nitrocellulose decomposition as the temperature is decreased was also found in the investigations of Svetlov and Lur'ye [43], who studied the decomposition of nitrocellulose without evacuation of gaseous products over a broader temperature range (70-140°C) at high values of δ (0.03-0.06). The increase in acceleration of decomposition as the temperature was decreased is shown on Figure 23, on which the abscissa shows the gas volume, while the ordinate shows the ratio of the rate corresponding to the moment of separation of this quantity of gases to its initial value; at 70°C at the moment of separation of 4 cm³ gases, the rate increased by six times, while at 140°C it increased by only 1.7 times.

The dependence of the initial decomposition rate on temperature for peroxiline No. 2 ($12.3\% \text{ N}$) is expressed by the relationship $k = 10^{14.4} \exp(-38,500/RT)$. Peroxiline No. 1 ($13.35\% \text{ N}$) was decomposed in the temperature interval $70-160^\circ\text{C}$ approximately twice as rapidly; $k = 10^{15.35} \exp(-39,500/RT)$, which is similar to the data produced by Samsonov at $100-170^\circ\text{C}$ and low δ . Acceleration of decomposition with time for peroxiline No. 1 was expressed more strongly (2-2.5 times) than for peroxiline No. 2.

In spite of the fact that acceleration of decomposition of nitrocellulose increases with decreasing temperature, the increase in the rate, if secondary effects such as self-heating are excluded, is not so great as was observed for nitroesters such as nitroglycerin, PETN, etc. Apparently, the possibility of self-acceleration of decomposition of nitrocellulose is more limited. This is confirmed also by a comparison of the rates of gas formation produced without evacuating the gaseous products with quasiconstant pressure and in a vacuum, where the maximum pressures differed by many orders, while the rates of gas formation differed by but a few times.

The increase in rate with time right up to the maximum [44] can be expressed by the relationship

$$\frac{dp}{dt} = Ae^{pt},$$

where A is a constant, depending on temperature; p depends on temperature and on δ . At 120°C and $\delta = 8 \cdot 10^{-4}$, if the rate is expressed in cubic centimeters per gram per second, the constants A and p are valued at $1.49 \cdot 10^{-4}$ and $1.34 \cdot 10^{-6}$ respectively.

In the light of the data produced, it is probable that the influence of the gaseous decomposition products on the course of decomposition depends primarily upon the interaction of their reactive components with each other and with the solid material, leading to an acceleration of gas formation and the formation of addition quantities of gas.

A comparison of various rates at various temperatures allows us to calculate the kinetic coefficients of the corresponding processes. In calculating the activation energy for reactions leading to losses in weight, the coefficients which matched the integral curves produced at various temperatures were used.

Using the initial rate of weight loss and the activation energy, we calculated the factor before the exponent, the logarithm of which was 17.8. The activation energy for the total gas formation and the formation of condensing gases was calculated from the course of the lines produced in coordinates $\log k = 1/T$. The activation energy for gases difficult to condense was calculated from the line $\log k_{\text{match}} - 1/T$ on the basis of matching of differential curves $\Delta v/\Delta \tau = f(t)$. The results of the calculations are shown in Table 2 and represented graphically on Figure 24.

Table 2
Kinetic coefficients of reaction rates for thermal decomposition of nitrocellulose in a vacuum at $135-160^\circ\text{C}$

Characteristics of reactions used to calculate rate constant.	Initial values of rate constants (k), $\text{sec}^{-1} \cdot 10^5$			E, cal/mol	log B, sec^{-1}	Method of calculating E
	135°C	145°C	150°C			
Weight loss*	0.090	0.33	0.65	2.4	17.8	By matching weight loss vs time curves
Gas formation	0.18	0.60	1.1	3.3	17.5	From initial gas formation rates
Formation of condensing gases	0.24	0.77	1.5	4.9	16.9	Same
Formation of gases difficult to condense	0.019	0.064	0.16	0.50	17.8	By matching curves in coordinates $\Delta v/\Delta \tau = f(\tau)$
Gas liberation without evacuation**	0.10	0.40	—	1.9	15.0	By matching curves $p = f(\tau)$

*Weight loss rate constant calculated relative to weight loss at τ_{∞} for gas formation relative to gas volume separated at τ_{∞} .

**Experiments performed at $100-170^\circ\text{C}$.

The values of activation energy and the factor before the exponent for all of the types of gases trapped and the weight loss are similar to each other. The data for the gas formation rate in a vacuum practically correspond to those produced by calculations using the data of Ville for the rate of separation of nitrogen compounds in a current of inert gas. Value of activation energy is somewhat greater than for the simplest alkyl nitrates and corresponds to that

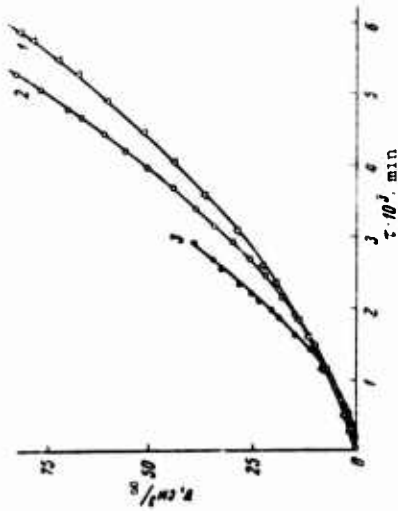


Figure 25. Influence of water on thermal decomposition of nitrocellulose at 120°C ($m/v = 50 \cdot 70 \cdot 10^{-4}$ g/cm³) at various water vapor pressures (mm Hg): 1, 0; 2, 138; 3, 663.

of nitroglycerin. This factor, and the increased value of the factor before the exponent in combination with the character of the change in rate with time analyzed above indicate that the formation of various types of gases as nitrocellulose decomposes is a result of the combination of several reactions and cannot be directly used for calculation of kinetic parameters of the individual reactions.

The decomposition of nitrocellulose was also studied in the presence of certain materials which are formed during the decomposition (water, nitrogen oxide and dioxide, nitric acid). Also, the influence of oxygen and sulfuric acid on the decomposition was determined.

Coujon and other investigators [45, 46], in studying the decomposition of moist nitrocellulose, observed a significant pressure drop after a certain induction period with a subsequent sharp increase in the rate of gas formation. However, in these experiments the nitrocellulose was in contact with air, which might complicate the picture of the influence of water. Actually, the experiments performed in the presence of water alone [47] showed that the nature of the decomposition does not change, and that its acceleration is considerably less than in the experiments of Coujon (Figure 25).

The situation is otherwise if, in addition to water, oxygen is present (Figure 26). The pressure remains almost unchanged for a long time, then drops rapidly and begins to climb just as rapidly; the rate increases by 100-150 times in comparison to that observed without these additives; this rapid gas formation is accompanied by brown coloration of the gas phase. The acceleration of decomposition of nitrocellulose is observed also in the presence of oxygen alone, without water, but the course of change in pressure in this case is different (Figure 27) and its increase is not so sharp. Apparently, in the presence of water and oxygen at first slow decomposition occurs and a small quantity of noncondensing gases is accumulated. At the same time, the water vapor is partially bonded to the condensed phase, so that the pressure over the nitrocellulose remains almost constant during the induction period, i.e. the quantity of condensing gases is correspondingly decreased. After a certain concentration of intermediate products is reached, a sharp drop in the pressure occurs, apparently due to an interaction of the water with the nitrocellulose and absorption of the nitric acid and water thus formed; the products of hydrolysis enter into oxidation-reduction reaction, accompanied by rapidly accelerating gas formation.

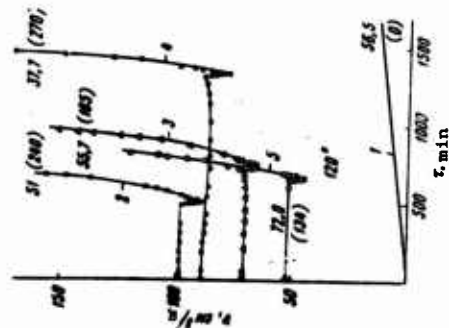


Figure 26. Combined influence of water and oxygen on thermal decomposition of nitrocellulose at 120°C with various $m/v \cdot 10^4$ ratios (numbers by curves). In parentheses by curves--pressure of water vapor in mm Hg; oxygen pressure (in mm Hg): 1, 0; 2, 63.5; 3, 264; 4, 87; 5, 274.

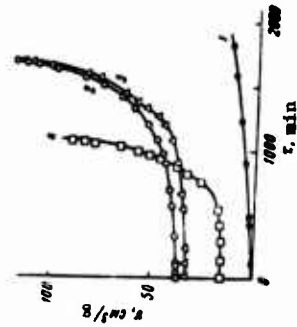


Figure 27. Influence of oxygen on thermal decomposition of nitrocellulose at 120°C ($m/v = 60-80 \cdot 10^{-4} \text{ g/cm}^3$) with various oxygen pressures (in mm Hg): 1, 0; 2, 267; 3, 265; 4, 168.5.

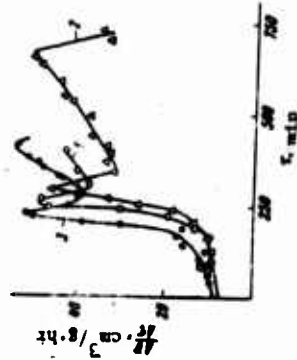


Figure 29. Influence of nitric acid at low concentration on thermal decomposition of nitrocellulose at 120°C. 1, 2.38% acid, 16.3% concentration; 2, 1.31% acid, 11.3% concentration; 3, 1.89% acid, 10.3% concentration.

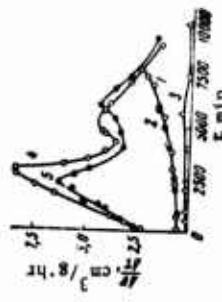


Figure 28. Influence of nitrogen dioxide content on rate of decomposition of nitrocellulose at 120°C. 1, without additives, $m/v = 13 \cdot 10^{-4} \text{ g/cm}^3$; 2, with 2% NO_2 at $P_{\text{NO}_2} = 55 \text{ mm Hg}$, $m/v = 56.1 \cdot 10^{-4} \text{ g/cm}^3$; 3, with 2% NO_2 in the presence of P_2O_5 , $m/v = 46 \cdot 10^{-4} \text{ g/cm}^3$, $P_{\text{NO}_2} = 22 \text{ mm Hg}$; 4, $m/v = 13.7 \cdot 10^{-4} \text{ g/cm}^3$, $P_{\text{NO}_2} = 275 \text{ mm Hg}$; 5, $m/v = 17.5 \cdot 10^{-4} \text{ g/cm}^3$, $P_{\text{NO}_2} = 218 \text{ mm Hg}$.

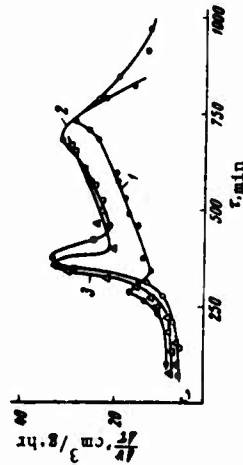


Figure 30. Influence of nitric acid at high concentration on thermal decomposition of nitrocellulose at 120°C. 1, 73.2% acid; 2, 2.76% of 43.7% acid; 3, 2.26% of 42.1% acid.

Dry nitrogen dioxide at low concentrations ($P_{\text{NO}_2} = 55 \text{ mm}$, $m/v = 56 \cdot 10^{-4} \text{ g/cm}^3$) accelerates the decomposition of nitrocellulose slightly; as the concentration is increased, the acceleration increases (Figure 28). Two maxima can be observed on the curve of rate of gas separation at high NO_2 contents. The first is higher than the second and is accompanied by complete decoloration of the gas phase. The increase in the initial rate in the presence of NO_2 can be explained by its oxidizing influence. However, the acceleration of gas formation develops slowly. One possible reason for this is the accumulation of NO : its presence in the case of decomposition of nitrocellulose reinforced the influence of the nitrogen dioxide. The decrease in rate after the maximum can be naturally related to exhausting the NO_2 . The second, relatively weak acceleration of gas formation apparently corresponds to that observed without additives; possibly, it is reinforced by hydrolysis due to the water formed in oxidation. The total volume of gaseous products in the presence of nitrogen dioxide increases by $30-40 \text{ cm}^3/\text{g}$.

The decomposition of nitrocellulose is also influenced by nitric oxide, although, naturally, considerably less strongly than by nitrogen dioxide. The initial rate is somewhat lower, but the acceleration is slightly greater than for nitrocellulose without additives.

In studying the influence of nitric acid on the decomposition of nitrocellulose, it was added in the form of an aqueous solution, the quantity of which amounted to 2% in relation to the nitrocellulose, and the concentration of the acid was varied from 0 to 100%. The curves of Figures 29 and 30 show that the nitric acid accelerated the decomposition of nitrocellulose. The greatest acceleration is provided by 10% acid; with lower and higher concentrations, its influence is less. The gas separation rate curves have two maxima; their values related to the concentration of nitric acid. At the first maximum of the curve, the brown coloration of the gases is most intense, while at the second maximum, complete decoloration of the gas phase is observed.

Concentrated (95%) sulfuric acid has an even stronger influence on the decomposition, this influence increasing with increasing δ . Figure 31 shows the dependence of the nature and rate of decomposition on the quantity of sulfuric acid⁷. Apparently, the nonvolatile sulfuric acid extracts nitric acid from the

⁷ See p. 131

nitrocellulose, subsequent decomposition of which leads to the development of oxidation-reduction processes, possibly accelerated by the sulfuric acid.

A comparison of experiments on the decomposition of nitrocellulose and nitroglycerin shows certain differences. In the decomposition of nitrocellulose where there is no water present, the acceleration is considerably less in order of magnitude than in the case of the decomposition of nitroglycerin. This difference can be assigned to one of two causes (for their combination)—a shortage of water or a shortage of acid for the development of hydrolysis. Experiments on the decomposition of nitrocellulose in the presence of water show that the first factor is not the determining factor. The presence of water does not change the characteristics of the curve, only slightly increasing the rate of gas formation. These experiments also show that the rate of reduction of the higher oxides of nitrogen produced in the decomposition in the presence of water, forming nitric acid, is rather high in experiments with nitrocellulose, sufficient to prevent the accumulation of the acid. In this respect, nitrocellulose is similar to diethylene glycol dinatrate, for which Svetlov also established the absence of an accelerating influence of water on the decomposition. However, the reducing properties of nitrocellulose under the decomposition conditions are not expressed as strongly and in the presence of oxygen, particularly in the combined presence of water and oxygen, the decomposition takes on the same nature as the decomposition of nitroglycerin. In the same way, the addition of nitric acid together with water leads to a strong increase in the rate of decomposition; if 2% acid is added (at 10% concentration), for example, the rate increases by 32 times at 120°.

It should be noted in conclusion that, since nitrocellulose is in the solid state at its decomposition temperature, topochemical decomposition is possible, involving the local formation and development of seeds. Some observations indicate that this assumption is correct. For example, Goujon [45] established that the rate of decomposition of nitrocellulose increases with a decrease in particle size, that is when the specific surface is increased. When nitrocellulose is decomposed beneath a layer of an inert liquid, the rate of decomposition decreases sharply, which also indicates the influence of the state of the surface on the development of the reaction. Finally, Mittasch [37] observed a unique influence of certain solid inert impurities on the decomposition, which was difficult to explain unless we assume an influence of the solidous surface on the development of the reaction.

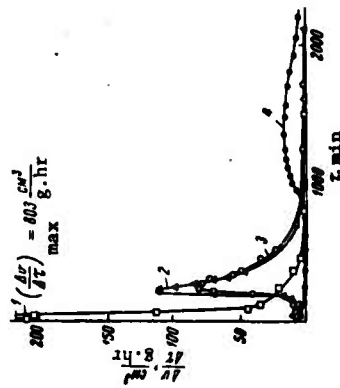


Figure 31. Influence of concentrated sulfuric acid on thermal decomposition of nitrocellulose at 100°C. Acid content (in %): 1, 3.55; 2, 1.57; 3, 1.26; 4, 0.51.

6. Gaseous Nitrites and Nitrates

The thermal decomposition of the nitrates of polyhydric alcohols is a complex process. One of the factors contributing to the complexity of this process is the formation of nitrogen dioxide as an intermediate product, which is an energetic oxidizer, interacting with the intermediate products, as well as with the nitrate itself, and also reacts with water to form acid. The oxidation process forms water, which, particularly in the presence of acid, rapidly hydrolyzes the nitroester; during liquid phase decomposition, the influence of hydrolysis is reflected to a varying degree on the course of the primary stages of decomposition. If we eliminate the conditions which favor the development of hydrolysis (i.e., by decomposing the nitroesters in the vapor phase at low pressures), the decomposition occurs kinetically considerably more simply.

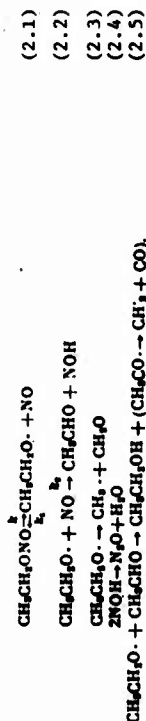
The complication of decomposition caused by nitrogen dioxide is also generally absent in the decomposition of nitrites, the primary product of which is nitric oxide in place of nitrogen dioxide (a much weaker oxidizer); otherwise, similarity in the nature of the decomposition to nitrates should be expected in its initial stages.

On the basis of these conditions, the thermal decomposition of mono- and polynitrites was studied, as well as the thermal decomposition of the nitrates of certain alcohols, in the gas phase.

Alcohol Polynitrites

The thermal decomposition of alkylnitrites (methyl, ethyl, n-propyl, isopropyl, n-butyl) in vapor phase is primarily homogeneous and the increase in pressure follows the first order reaction rule [48]. The activation energy for all members of the series is almost identical, about 37 kcal/mol.

The explanation of these dependences, as well as the composition of the decomposition products and the influence of various impurities can be given for ethylnitrite on the basis of the following decomposition mechanism, including the reversible separation of the NO-group [49] as a first stage.



The rate of disappearance of the initial material is

$$-\frac{d[\text{C}_2\text{H}_5\text{ONO}]}{dt} = \frac{k_1 k_3}{k_1 + k_2} = K. \quad (2.6)$$

For dinitrites [50] at comparatively high temperatures (~300°C), the first stage of the decomposition is also the formation of NO and the oxyradical. The further fate of the oxyradical (decomposition of regrouping with the NO₂ fragment) depends on its structure.

An investigation of the thermal decomposition of ethylene glycol dinitrate in the vapor phase (b.p. 96°C) was performed by Kondrikov using a manometric method at 120-190°C with initial pressures of 50-1000 mm [51-53].

The principal feature of the decomposition of this material is the clearly expressed two-staged nature of the process (Figure 32) which is more strongly manifest the higher the pressure and the lower the temperature. At very high pressures and low temperatures, the second stage begins so early that the curve of p(t) takes on the ordinary S-shaped form observed in an autocatalytic reaction. The initial rate (at 170°C) does not depend on the concentration⁸, and at low pressures, the decrease in rate with time occurs approximately according to the first order reaction rule. The total time of decomposition with

⁸ See p. 131

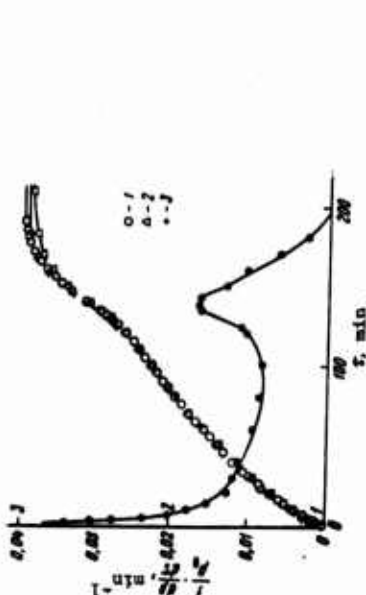


Figure 32. Kinetics of gas formation in the decomposition of glycol dinitrite at 170°C; initial pressure (in mm Hg). 1, 248; 2, 248; 3, 251, curve with maximum--in coordinates 1/p₀ · dp/dt - τ; value of p/p₀ on ordinate to right.



Figure 33. Influence of initial concentration on decomposition of glycol dinitrite at 170°C with various pressures (in mm Hg): 1, 76; 2, 221; 3, 320; 4, 405 and 5, 659.

high initial pressures is considerably reduced due to an increase in the share of the second stage reaction (Figure 33). The initial rate at 170°C is $5.8 \cdot 10^{-4} \text{ sec}^{-1}$; its increase with temperature indicates an activation energy of 35.6 kcal/mol. The addition of nitric oxide essentially decreases the initial pressure increase rate (although only to a certain point), but does not influence the rate of the second stage of decomposition. Analysis of the gaseous end product at 170° (their quantity and the experimental temperature amounting to ~3 moles per mole of nitrate) shows that their principal component part is nitric oxide (about 3/4), followed by CO₂, CO, N₂O and N₂. As an intermediate product at high concentrations of dinitrite or at low temperatures, nitrogen dioxide is detected (by a yellowing of the gas phase). In the condensed products—a colorless viscous liquid, which dissolves well in water and produces an acid reaction to litmus, glycolic acid, water, formaldehyde and, apparently, glycolic aldehyde were detected qualitatively.

The nonvolatile products were produced exclusively during the second stage, and an increase in the pressure influences their formation only to the extent to which it influences the course of the second stage of the reaction. The addition of water and addition of surface by packing the vessel with glass tubes had no influence on the rate of the initial stages, but did accelerate the second stage reaction. The decomposition products which condense at room temperature (particularly in combination with water), have an even stronger influence.

The similarity of the activation energy of the initial stage to values produced for mononitrites (Table 3) the formation of NO and N₂O, the similarity in the nature of the influence of NO on the first stage with that observed for isopropyl nitrite [49] lead us to the conclusion that the mechanism of the first stage is similar to that assumed for that of mononitrites:



In the presence of NO₂, the following reaction is also possible:



Table 3

Rate of thermal decomposition of alkyl nitrites

Material	Temperature interval, °C	Activation Energy E, kcal/mol	Log E, sec	Initial decomposition rate and k at 190°C, sec ⁻¹ · 10 ⁴
Methyl nitrite	190-241	36.4	13.26	0.97; 0.48
Ethyl nitrite	190-241	37.7	14.14	1.89; 0.94
n-propyl nitrite	161-201	37.5	13.79	
isopropyl nitrite	170-210	34.3 ± 3		3.95; 1.98
n-butyl nitrite	200-230	34.7	14.44	
isopropyl nitrite	170-210	37.0	13.20	3.70; 1.85
ethylene glycol dinitrite	170-212	37.0	14.10	8.88; 4.44
glycerol trinitrite	202-239	36.2	13.66	33; 11
	170-190	35.6	13.8	
	143-160	41.6	17.8	140*; 47

*Calculated.

Assuming that the concentration of the CH₃ONOCH₂O radical concentration is stable, we produce the following for the rate of change in pressure

$$\frac{dp}{dt} = k \frac{k_2[\text{NO}]}{(k_1 + k_2)[\text{NO}] + k_3} \left[\frac{\text{CH}_3\text{ONO}}{\text{CH}_3\text{ONO}} \right] \quad (2.12)$$

For the initial rate of gas formation during decomposition we have

$$W_0 = \frac{1}{k} \left(\frac{dp}{dt} \right)_0 = 3k \quad \text{or} \quad k = \frac{1}{3} W_0 \quad (2.13)$$

This agrees with its independence on concentration and allows us to determine the rate constants from the initial rates of gas formation, as well as the constants B and E for the Arrhenius equation for k

$$k = 10^{13.5} \exp(-35600/RT) \text{ sec}^{-1}$$

For experiments with the addition of nitric oxide, the initial gas formation rate is determined by the expression

$$W_0^{\text{NO}} = \frac{1}{k} \left(\frac{dp}{dt} \right)_0 = k \frac{k_2[\text{NO}]}{(k_1 + k_2)[\text{NO}] + k_3} \quad (2.14)$$

It follows from this expression, as experiments have shown, that the initial rate depends only on the concentration of NO and as it is increased approaches the limit $kk_2/k_1 + k_2$.

Analysis of experimental data allows us to calculate the relationship of the rate constants of secondary reactions in the first stage: $k_2/k_1 \sim 6$; $k_3/k_1 \sim 120$ (concentration given in mm Hg). Also, the self-retardation of the reaction in the first stage and its dependence on the initial dinitrite concentration are explained.

Kondrikov looks upon the second stage of decomposition as the interaction of glycol dinitrite and, possibly, the intermediate products of its decomposition with water, first formed, for example, by the reaction $2\text{NOH} + \text{N}_2\text{O} + \text{H}_2\text{O}$. This leads to replacement of the nitrite group with an oxy group and the formation of nitric acid, which is decomposed into the oxide and dioxide of nitrogen and water. The nitrogen dioxide oxidizes the organic products, forming CO , CO_2 and water. General considerations, as well as the influence of the surface and the nonvolatile products indicate that these reactions occur in a thin film of liquid covering the wall of the vessel.

The decomposition of glycerin trinitrite was studied at 100-160°C. The similarity of the kinetic curves (Figure 34) and regularities with those produced for glycol dinitrite is great: independence of the initial rate on concentration, increase of maximum rate with increasing concentration and decreased time required to achieve it, increased role of second stage reactions with decreased temperature, decrease in initial rate when NO is added and absence of the influence of NO on the second stage, accelerating influence of condensed decomposition products and water, influence of surface on the second stage, and absence of this influence on the first stage.

There are, however, certain differences. With similar complete decomposition times, the role of the second stage reaction in the decomposition of trinitrite is considerably greater. The rate during the first stage decreases less sharply and the depressing influence of initial concentration of the rate of the first stages of decomposition does not appear. The yellow coloration of the gas phase is more strongly expressed, particularly at low temperatures.

With a significant decrease in temperature (up to 100-120°C), the nature of the curve of $p(t)$ changes slightly; the rate does not decrease in the initial stage, but rather increases slowly, as usually occurs in an autocatalytic reaction, and was observed for glycol dinitrite under the same conditions.

The kinetic characteristics of the decomposition of various nitrites are presented in Table 3. We can see from Table 3 that an increase in the molecule in the series of alkyl mononitrites leads to an increase in the decomposition rate. As we go from one homolog to the next, the reaction rate increases by a factor of approximately 2. As the complexity of the molecule increases, the rate of decomposition of the oxyradical, which has almost no role to play in the decomposition of ethyl nitrite but a very important role to play in the decomposition of n-propyl nitrite, also increases.

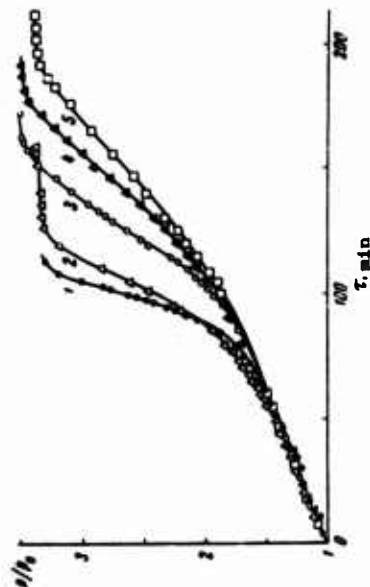


Figure 34. Kinetics of gas formation in the decomposition of glycerin trinitrite (temperature 150°C) at various initial pressures (in mm Hg): 1, 545; 2, 310; 3, 215; 4, 142; 5, 69.

If the molecule of ethyl nitrite is made more complex by replacing the hydrogen of the β -carbon atom by O-NO , i.e., if the ethyl nitrite is converted to ethylene glycol dinitrite, in the initial stage of the decomposition this leads to an increase in the rate of bursting of the O-NO bond by 5-6 times more than when the CH_3 -group is introduced, as well as to some increase in the rate of decomposition of the oxyradical without any change in principle in the mechanism of this stage.

The same thing occurs upon transition from propyl nitrite to glycerin trinitrite: the principal reactions in the initial stage of the decomposition are retained, but the rate with which the O-NO bond is broken and the rate of decomposition of oxyradicals are essentially increased.

When the temperature is increased, the relationship between individual rates obviously changes. The rate of decomposition of the oxyradical, probably, increases more rapidly than the rate of the reaction between this radical and the nitric oxide.

Thus, if we look upon the initial stage of the process alone, the transition from mononitrites to polynitrites causes no basic changes in the decomposition mechanism. Naturally, the rate of individual main reactions and the relationships between the constants of these rates change, primarily in the decomposition of the oxyradical and in its reactions with the nitric oxide (not in favor of the latter). However, if we go over to analysis of the entire process of decomposition as a whole, we discover the essential basic difference in the mechanism of gas phase pyrolysis of polynitrites from that of mononitrites. It consists of the presence of a second, self-accelerating and essentially polymolecular stage in the decomposition of polynitrites under certain conditions, as well as the appearance in the intermediate products of nitrogen dioxide, closely related to the degree of development of this self-accelerating reaction.

The most probable explanation of the mechanism of the second stage is that the polynitrites, with their great tendency toward hydrolysis, decompose on the walls of the vessel in the film of nonvolatile decomposition products which covers the wall. The nitric acid thus formed decomposes rapidly, forming nitrogen dioxide, which aids the oxidation reaction, yielding the organic acids and carbon dioxide determined in the end products.



Figure 35. Change of pressure of gaseous products (1) and rate of decomposition (2) of nitroglycerin with time in vapor phase at 140°C.

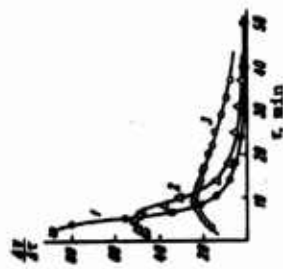


Figure 36. Change of rate of gas formation with time during decomposition of PETN (171°C) with small δ : 10^4 : 1, 0.43; 2, 0.83; 3, 11.4.

The transition from alkyl mononitrites to ethylene glycol dinitrite and glycerin trinitrite increases not only and not so much the rate of thermal decomposition, as the rate of hydrolysis of the nitrite. Apparently, an essential role here is played by the decomposition of nitrite groups in contact with each other. The share of the second stage of the reaction is considerably less for 1,4-butylene glycol dinitrite, which does not differ in its rate of thermal decomposition from 1,2-ethylene glycol.

The decomposition of nitroglycerin in the vapor phase [13] was studied at 140, 150 and partially at 165°C with values of δ calculated from the dependence of the vapor tension on temperature. The absolute gas formation rate is proportional to the concentration of vapors, is several times higher than that of liquid nitroglycerin, and continuously decreases with time (Figure 35); whose decrease differs in its characteristics from that which is characteristic of first order reactions. When the reaction vessel is filled with glass capillaries (surface increased by a factor of 7), the rate is increased by 2-3 times, indicating that a heterogeneous reaction occurs on the glass at the same time as the homogeneous reaction. The gaseous decomposition products, first colorless, become brown, then once more lose their coloration; at the same time, the share of gases condensing at room temperature decreases.

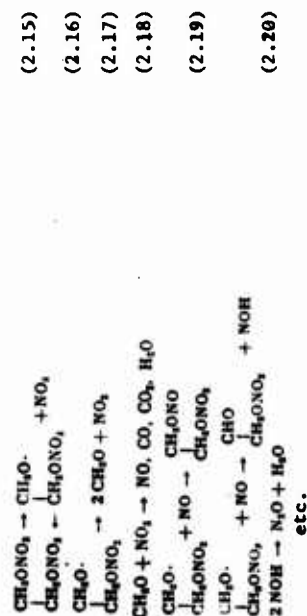
The decomposition of nitroglycerin vapors at 140-170°C occurs in generally similarly to the decomposition of nitroglycerin; the relative rate does not depend on the initial concentration, although it does increase somewhat at the beginning (in contrast to nitroglycerin) with time. The final gas volume increases as the experimental temperature rises. The curves of $p(t)$ match well over the 20-60% decomposition sector (percentage of final pressure) by varying the time scale, and the dependence of the transformation coefficient on temperature indicates an activation energy of 34.2 kcal/mol; it is less than for the liquid; for nitroglycerin vapors, the activation energy is considerably greater than for nitroglycerin vapors. Since the rate of decomposition is similar (at 140°C, nitroglycerin decomposes only 5 times more rapidly than nitroglycerol) the values of the factor before the exponent differ by the same amount.

The decomposition of PETN at 171°C was studied [31, 32] with small δ ($11 \cdot 10^{-4}$ - $0.4 \cdot 10^{-4}$), when a significant portion of the material is in the vapor state (Figure 36). The less δ , the less, as in the case of nitroglycerin, the acceleration of the decomposition and the greater its actual rate. Approximate

calculations show that PETN in the vapor state is decomposed 6-8 times more rapidly than in the liquid state.

Increasing the surface available in the decomposition of PETN and nitroglycerol does not change the rate of gas formation, indicating the absence of any notably heterogeneous reaction on the walls of the vessel. The results of investigation of the decomposition of glycol and glycerin polynitrates, as well as alkyl mononitrates, allow certain conclusions to be drawn concerning the decomposition of polynitrates.

The overall plan of this decomposition can be represented (as applicable to a simple dinitrate) in the form of a series of sequential reactions [53]:



In comparison with ethyl nitrate, the rate of decomposition of the oxynitradical will be greater, while the relationship of rate constants in the formation of nitrite nitrate and oxaldehyde nitrate change in favor of the latter. As a result, the peculiarity of the decomposition of ethyl nitrate consisting of the formation of a large quantity of nitrite as an intermediate product is apparently not characteristic for the decomposition of glycerin trinitrate and glycol dinitrate, at least in the temperature interval studied.

Individual data on the decomposition of polynitrates support this mechanism. The rate of decomposition of ethylene glycol dinitrate and nitroglycerin is independent of the initial concentration.

The activation energy in the decomposition of ethylene glycol dinitrate is similar to the activation energy of ethyl nitrate; when nitric oxide is added, the initial gas formation rate decreases (at 170°C), and its dependence on concentration is the same as for the dinitrite. NO has no influence on the later states. Nitric oxide is discovered in the decomposition products in the presence of NO.

The presence of a rate maximum for glycol dinitrate is possibly related to the accumulation of the intermediate product in considerable concentrations which, decomposing, forms gases. The absence of such a maximum in the decomposition of nitroglycerin may be related to the fact that the quasiequilibrium concentration of the intermediate product is not great and is achieved early. Attention is drawn in this respect by the increased activation energy and value of the factor before the exponent for glycerin nitrate and nitrite in combination with the increase rate constant of decomposition. There is no reason to expect an increase in the activation energy for the reaction of splitting of NO or NO₂ from the molecule in glycerin derivatives in comparison with glycol derivatives, in fact the opposite would be expected. Therefore, this peculiarity of the glycerin derivatives is probably related to the fact that the leading reaction is more complex than in the case of the decomposition of nitrates of dihydric alcohols and, possibly, consists of a combination of reversible endothermic decomposition of the molecule with formation of an intermediate product which irreversibly decomposes to form gases. Under these conditions we might produce the same regularities which have been established for glycerin trinitrate and trinitrite.

On the whole, the decomposition of nitrites has significant points of similarity to the decomposition of nitrates, particularly in the initial stage, which is qualitatively the same, consisting of the separation of NO- and NO₂-groups respectively. The differences result from the possibility of formation of water and acid as a participant in a catalyst of hydrolysis, which is the reason for the onset of the second stage. This possibility is greater for the nitrates. On the other hand, the relative ease of hydrolysis of nitrates, as well as the formation of nonvolatile liquid products (in the case of decomposition of nitrates, they are oxidized to gases) favors the onset of the second stage even under conditions under which it is not observed in the decomposition of nitrates (decomposition of vapors). At the same time, this stage is much more rapid and self-accelerating for nitrates, since the basic oxidizer and oxygen source (NO₂) is created in greater quantity than the nitrates can produce. Correspondingly, a considerable quantity of water is produced for continuation of hydrolysis.

The fact that it is hydrolysis which is the decisive factor in the strong acceleration of decomposition is clearly shown by the decomposition of nitro-

glycerin and methyl nitrate in the vapor phase: the oxidizer (NO_2) is formed in large quantities, but the self-acceleration of the process is still not observed. Therefore, it is the possibility of the development of hydrolysis, which depends on the availability of water, the rate constants of hydrolysis and the influence of acid, as well as the accumulation of acid, which define the degree of self-acceleration of decomposition. In turn, the accumulation of acid is possible if the nitrogen dioxide formed is not reduced too rapidly to the oxide. This last factor determines the strong difference in the tendency to self-acceleration of the decomposition of nitroesters such as nitro-glycerin and nitroesters as diethylene glycol dinat.

II. Nitromethane

The kinetics of thermal decomposition of nitromethane have been studied [54] statically and by a current method at various temperatures at low (4-400 mm) and high (12-40 atm) of pressure. The decomposition followed the first order reaction rule in both cases. At low pressure (4-400 mm) the order of the reaction increased slightly as the temperature was increased.

The study of the influence of various gases on decomposition at low pressures showed that for the most part they do not influence the decomposition (helium, nitrogen, nitric oxide, carbon dioxide, water); oxygen accelerates the decomposition, hydrogen slows it down; the addition of the oxide or dioxide of nitrogen at high pressures has no influence on the rate of decomposition, if the quantity involved is not great; at higher quantities, these compounds delay decomposition. Oxygen at high pressures has no influence on the rate of the reaction, although it changes the composition of the products. Free radicals decrease the decomposition at temperature of nitromethane.

The composition of the decomposition products differs essentially depending on the pressure at which decomposition is performed.

At low pressures (200-400 mm) and in the temperature interval 280-300°C, the decomposition products contain nitric oxide, nitrous oxide, water, carbon monoxide, methane, carbon dioxide, small quantities of ethene and ethane and traces of nitrogen dioxide. The principle nitrogen-containing compound is nitric oxide, the content of which decreases as the decomposition continues. The $\text{CO}:\text{CH}_4:\text{CO}_2$ ratio (10:6.2:1.4) remains constant after 5% decomposition of the nitromethane.

At increased pressures and 355°C, the principle products of decomposition are carbon dioxide, carbon monoxide, methane, hydrocyanic acid, nitric oxide, nitrogen, water and in smaller quantities methylcyanide, ethylcyanide, formaldehyde and nitrous oxide. At 5% decomposition, the $\text{CO}:\text{CH}_4:\text{CO}_2$ ratio was equal to 10:5:10. The most important difference in the composition of the decomposition products at high pressures is the formation of large quantities of hydrocyanic acid in the early stages as the principal carbon-containing product.

Two reactions have been suggested as the initial stage in the decomposition at low pressures: the decomposition of nitromethane into nitrosomethane and an oxygen atom, resulting from breakage of the bond between the nitrogen and one oxygen

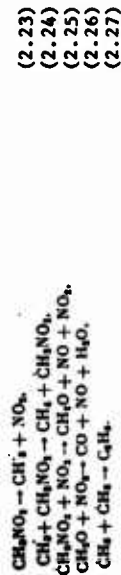


and decomposition to a methyl radical and nitrogen dioxide, involving the breakage of the bond between the nitrogen and carbon



Mechanism (2.21) is inapplicable to decomposition at low pressures, since it does not result in the formation of hydrocyanic acid, which is easily formed in the decomposition of nitrosomethane. On the other hand, the formation of free radicals and nitrogen dioxide speaks in favor of mechanism (2.22). The activation energies found in most investigations lie between 50 and 53 kcal/mol. The energy of the C-N bond, which is 57 kcal, is greater than the activation energy. This indicates the possibility of the radical decomposition mechanism. However, since the reaction is retarded only by large quantities of nitric oxide, the existence of only very short chains can be allowed.

The following reaction plan can be assumed for the initial stages at low pressures:



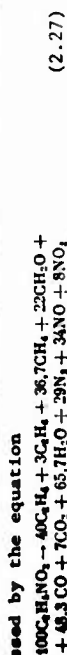
The formation of large quantities of HCN at high pressures can be explained by the formation of nitrosomethane according to reaction (2.21). However, it might also be formed by the interaction of the methyl radical with nitric oxide.

This reaction results from a triple collision; therefore its role is small at low pressures and becomes great at high pressures. This explanation is also favored by the fact that the quantity of hydrocyanic acid increases even at high pressures upon the addition of an inert admixture (CO_2); the addition of NO has the same effect.

Also, the influence of various oxides on the ignition of nitromethane has been studied; the basic oxides catalyze the reaction, in contrast to the acid oxides, which have no influence on it. Apparently, the acid-form of nitromethane has an essential role to play in the ignition, probably interacting with the basic oxides.

The decomposition of nitroethane and nitropropanes has been studied to a lesser extent than that of nitromethane. According to Gottrell, et al [55], in the temperature interval 355-405°C, nitroethane is decomposed primarily homogeneously at pressures of 50-300 mm according to the first order reaction rule. The share of the heterogeneous reaction under these conditions, which increases as the temperature drops, is about 10%. The addition of nitric oxide has no influence on the reaction rate. Principal gaseous reaction products are ethylene and nitric oxide. According to energetic considerations, and also considering the formation of the olefin, the authors exclude splitting of the nitrogen dioxide and assume intramolecular regrouping with subsequent monomolecular decomposition to the olefin and nitric acid, which then rapidly decomposes to water, nitric oxide and nitrogen dioxide, which oxidizes the olefin.

Gray, et al [56] established the formation of free radicals in the decomposition of nitroethane, as well as a considerable acceleration of its decomposition upon introduction of methyl radicals. In addition to this, the composition of the decomposition products is more complex than would be expected, if the first reaction consisted only of intramolecular splitting of HNO_2 . At 477°C, decomposition can be expressed by the equation



All this indicates that the primary stage is decomposition of the nitroalkane into the radical and NO_2 . This reaction can explain the subsequent formation of all remaining experimentally determined products--ethylene, nitric oxide, CO , formaldehyde and methane.

The products of primary decomposition interact also with the nitroethane itself, as a result of which the observed rate of decomposition is greater than the rate of breakage of the CN -bond. The activation energy is 39 kcal/mol, which is considerably less than the energy of this bond. For 1-nitropropane, an activation energy of 48.5 kcal/mol has been produced, although this result cannot be considered precise, while for 2-nitropropane $E = 39$ kcal/mol. Otherwise, the decomposition of nitropropanes is similar to the decomposition of nitroethane.

The usage of nitromethane as a rocket fuel is complicated by the necessity of using a longer chamber than for other fuels. This apparently results from the slow combustion of nitromethane, which can be accelerated by using Cr_2O_3 or Fe_2O_3 as a catalyst. A study of the decomposition of nitromethane in the presence of catalysts was performed in the temperature interval 220-245°C with an initial pressure of 36 atm [57]. Ferric oxide (in contrast to chromic oxide) loses its catalytic activity after decomposition if 1/3 complete.

In the presence of chromic oxide, decomposition occurs according to the first order reaction equation:

$$k = 10^{11} \exp(-36000/RT).$$

One difference of catalytic decomposition is the high decomposition rate corresponding to the various values of lower activation energy (36 and 49.2 kcal/mol. Also, the decomposition products contain no hydrocyanic acid, which is contained in various quantities (depending on pressure) in the products of noncatalytic decomposition. Another difference is the content of large quantities of ammonium bicarbonate (particularly at high pressures) and the absence of the solid black residue which is present in large quantities without the catalyst.

These differences can be explained by the two different decomposition mechanisms. One of them assumes the same reaction as a first stage and occurs with noncatalytic decomposition--breakage of the C-N bond.

In order to explain the formation of ammonium bicarbonate and the absence of HCN , it must be assumed that the latter is completely hydrolyzed in the presence of oxygen to form carbon monoxide and ammonia, which then forms bicarbonate with water and carbon dioxide.

This explanation has been confirmed by heating HCN with water with and without

the catalyst at 230°C. Without the catalyst, the hydrolysis did not occur, while with the catalyst ammonia was formed. The second mechanism assumed as a first stage is breakage of the N-O bond to form methyloxime and hydroxyl.

The influence of catalysts can be compared to the influence of oxygen, which also leads to disappearance of the HCN from the decomposition products and, like it, requires the minimum permissible combustion chamber length. Apparently, the greater significance of chamber length when nitromethane is burned results from the slow nature of the decomposition of HCN.

III. Aromatic nitrogen compounds

The first attempts at a comparative evaluation of the rates of thermal decomposition of nitro-compounds in the aromatic series were made by Farmer and Robertson. Farmer [58] determined the temperatures at which 1 g of explosive liberated 1 cm³ of gases in 100 hours (Table 4). Robertson [59] established the rate of gas formation at a certain constant temperature (140 and partially 120°C) for the same purpose (Table 5).

Table 4

Explosive	M.P., °C	Temperature, °C
Trinitrobenzene	123	190-195
Trinitrophenol	122.5	150-155
2,4,6-Trinitrotoluene	80.6	135-140
2,3,4-Trinitrotoluene	110.3	135-140
2,4,5-Trinitrotoluene	102.3	130-135
Tetryl	129	115-120
Cellulose nitrate (13% N)	-	100

The data from these works show that the nitro-compounds are much more stable than nitroesters and, as a rule, than nitroamines as well. Of the trinitro-compounds, trinitrobenzene decomposes much more slowly than the others, while trinitroacetone and trinitroxyloxy approach it. Apparently, the low rate of decomposition of the latter two nitro-compounds results to the considerable extent from the fact that they are in the solid state at the experimental temperature. The asymmetrical isomers of trinitrotoluene and trinitrobenzene decompose generally considerably more rapidly than the symmetrical isomers.

A systematic study of the kinetics of thermal decomposition of many nitro-compounds (mono-, di- and trinitrobenzene and a number of derivatives of the latter, including the methyl-, oxy-, dioxy-, nitro-, chloro-, dichloro-, tri-chloro- and amino-derivatives) was recently performed by Maksimov [60] and partially (for trinitrophenol and trinitroresorcinol) by L. Yu. Bao-fen [61, 62].

For most compounds, decomposition was performed both in the liquid phase and in the vapor phase, while for compounds with high vapor tension and low decomposition rate constant (mono- and dinitrobenzene) decomposition was performed only in the vapor phase, and for compounds with very low vapor tension and high melting point it was performed in the melted state (or in a solution) and in the solid state.

Table 5

Rate of gas formation W (in cm³/kg-hr) upon decomposition of certain explosives

Explosives	M.P., °C	Rate of gas formation after 40 hours, heated				
		80°	120°	140°	160°	180°
1,3-dinitrobenzene	90	-	-	0*	-	-
2,4-dinitroaniline	127	-	-	0*	-	-
1,3,5-trinitrobenzene	123	-	-	0*	-	0.05
1,4,6-trinitroacetone	235	-	-	0.003	-	8.4
2,4,6-trinitro-m-xylene	182	-	-	0.5	8.0	-
2,4,6-trinitrophenol	122.5	-	-	0.6	-	-
2,4,6-trinitroaniline	198	-	-	4	-	-
1,2,4-trinitrobenzene	61	-	-	8	-	-
2,4,6-trinitrotoluene	80.6	-	-	9	-	-
2,4,6-trinitro-m-cresol	109.5	-	-	10	-	-
2,3,4-trinitrotoluene	110.3	-	-	13	-	-
2,3,5-trinitrotoluene	92.5	-	1.5	24**	-	-
2,4,5-trinitrotoluene	102.3	-	-	32	-	-
2,4,6-trinitroanisol	68.4	-	-	32	-	-
Tetryl	129	-	3	128**	-	-
2,3,4,6-tetranitroaniline	217	-	18	288**	-	-
3,4,5-trinitrotoluene	132	-	22	352**	-	-
Oxytetryl	182	-	23	370**	-	-
Nitrocellulose (13% N)	-	-	2500 (135°)	5000**	-	-
Nitroglycerin	13.3	-	1660 (115°)	86000**	-	-
Lead azide	-	-	-	-	-	40
Mercury fulminate	-	2.5	-	-	-	-

*Rate cannot be measured at 140°C.

**Rate of gas formation at early stage of decomposition before acceleration.

1. Decomposition of Nitro-Compounds in the Vapor Phase Mono-, Di- and Trinitrobenzene

The decomposition of mononitrobenzene was studied in the vapor phase in the area of initial pressures between 80 and 1150 mm at 416°, the decomposition of dinitrobenzene--from 190 to 740 mm (95°C), that of trinitrobenzene--from 90 to 250 mm. These data were used for a determination of the influence of concentration on the decomposition rate and its change with time. The dependence of the decomposition rate on temperature was studied in the temperature intervals 390-415° (mononitrobenzene), 345-410° (dinitrobenzene) and 270-355°C (trinitrobenzene).

Decomposition occurs with the formation of gases, the final pressure of which exceeds the initial pressure by a factor of 2 (mononitrobenzene), 3 (dinitrobenzene) and 4.5 (trinitrobenzene). At the same time, condensed products are formed, in the greatest quantity for the mononitro-compound.

Throughout the entire temperature interval studied, the relative rate of pressure increase for dinitrobenzene was greater than for mononitrobenzene, and was greater for trinitrobenzene than for dinitrobenzene. At 350°C and $P_0 = 500$ mm dinitrobenzene is decomposed 1.6 times more rapidly than mononitrobenzene at 1000 mm; at the same temperature trinitrobenzene ($P_0 = 200$ mm) is decomposed 20 times more rapidly than dinitrobenzene (at $P_0 = 500$ mm).

The initial rate and nature of the pressure increase curve with time depend on the initial vapor pressure. In mononitrobenzene as the initial pressure increases, the initial rate increases, apparently approaching a certain limit. (Figure 37); the rate decreases with time, and for small pressure (about 100 mm) it follows the first order reaction rule, while at higher pressures the rate decreases more slowly at the beginning of the experiment (Figure 38).

For dinitrobenzene, the initial rate also increases with increasing initial pressure, but it reaches its maximum value earlier (at lower pressure) than with mononitrobenzene; the qualitative difference from mononitrobenzene is that even at the lowest of the pressures studied the rate increases with time, more strongly the higher the initial pressure (Figure 39).

9 See p. 131.

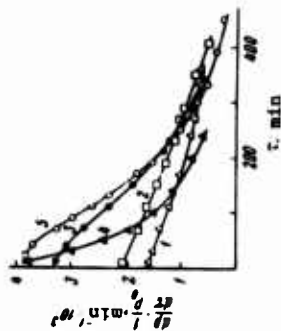


Figure 38. Change in rate of gas formation upon decomposition of mononitrobenzene (temperature 415°C) with initial pressure (mm Hg): 1, 80; 2, 215; 3, 575; 4, 1000; 5, 1150.

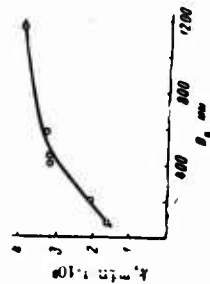


Figure 37. Influence of vapor pressure of mononitrobenzene on initial relative rate of decomposition at 415°C.

With trinitrobenzene at pressures from 92 to 250 mm (Figure 40) the initial rate remains constant; apparently, its increase with pressure, if such an increase does occur, occurs in the area of even smaller pressure than for dinitrobenzene and particularly for mononitrobenzene. The acceleration of gas formation with time is expressed even more strongly than for dinitrobenzene.

It is possible that these differences between mono-, di- and trinitrobenzene are related to a certain extent with the fact that the experiments were performed at different relative pressures ($P_{rel} = P_0/P_s$, where P_s is the saturated vapor pressure). For example, for mononitrobenzene at 416°C, the delay in the rate decrease, which is absent at $P_0 = 80$ mm ($P_0/P_s = 0.004$) becomes noticeable at 1150 mm ($P_0/P_s = 0.05$); probably at even higher pressures the acceleration of gas formation would be observed similar to that which occurs in the decomposition of dinitrobenzene at 395°C and $P_0 = 185$ mm ($P_0/P_s = 0.03$). The relative acceleration observed for trinitrobenzene at $P_0 = 92$ mm ($P_0/P_s = 0.29$) is possibly related to some extent with the fact that the experiments were performed at relatively low temperature, when the processes of acceleration are expressed much more strongly than at higher temperatures (at 312°C, for example, $W_{max}/W_0 = 4.5$, while at 355°C and the same initial pressure it is only 1.5).

Increasing the surface of the vessel (by placing capillaries in it) has an essential influence on the nature of the curve $p(t)$ and on the initial rate also, the final gas volume is decreased. In mononitrobenzene, the delay in the rate drop disappears, while with trinitrobenzene the maximum disappears; the initial rate sharply increases, and the rate drops continually with time according to a rule near the first order reaction rule. The curve of $p(t)$ for dinitrobenzene with increased vessel surface differs in form from the curves for mononitrobenzene and trinitrobenzene, but this difference consists primarily in that a sector of initial rate increase is noted, which was not noted under the experimental conditions with mononitrobenzene and trinitrobenzene.

The regularities produced can be explained qualitatively by assuming that under the conditions of the experiments as the nitrobenzene vapors decompose both the homogeneous reaction and a heterogeneous reaction occur on the glass with comparable speeds; the specific share of the heterogeneous reaction increases upon transition from mononitrobenzene to dinitrobenzene and trinitrobenzene. The homogeneous reaction occurs with an acceleration which is weakly expressed in mononitrobenzene, more strongly for dinitrobenzene and still more strongly for trinitrobenzene; the rate of the heterogeneous reaction, which possibly occurs without an acceleration, decreases according to a rule near the first order reaction rule; as the pressure increases, the specific share of the homogeneous reaction increases, the rate maximum becomes greater and begins earlier.

The dependence of the reaction rate on temperature was determined for mononitrobenzene by constructing an Arrhenius line, the rate constant being calculated for the initial factor of the curves

$$\frac{dp}{dt} \frac{1}{P_0} - t$$

(value of P_0 was varied for the experiments being compared over a relatively narrow range—from 300 to 500 mm).

From the graphs constructed the value of $E = 53.4$ kcal/mol and $\log B = 12.65$. Analogously for dinitrobenzene $E = 52.6$ kcal/mol and $\log B = 12.70$; for trinitrobenzene $E = 51.9$ kcal/mol, $\log B = 13.6$

Of course, with simultaneous occurrence and comparable rates of the heterogeneous and homogeneous reactions, the specific share of which changes with

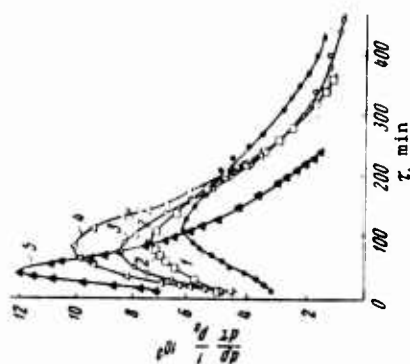


Figure 39. Change in rate of gas formation with time upon decomposition of 1,3-dinitrobenzene in the vapor phase (temperature 395°C) at various pressures (in mm Hg): 1, 1.185; 2, 2.307; 3, 3.450; 4, 4.740; 5, 5.666 (glass surface increased by 10 times).

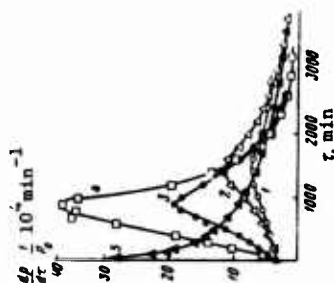


Figure 40. Change in rate of gas formation with time in decomposition of trinitrobenzene in vapor phase (312°C) at various pressures (in mm Hg): 1, 1.92; 2, 2.137; 3, 2.30; 4, 2.47; 5, 1.35 (glass surface increased by 10 times).

temperature, this method of calculation is only a formal method as concerns the summary rate, particularly since when the absolute initial pressures are equal, the relative pressures were different for the three compounds; their capability to adsorb under glass might have also been different. With this restriction, we can use the data produced to conclude that at identical temperatures, the temperature rate factor is approximately the same for all three materials, which is expressed by the approximately identical value of E .

The temperature also influences the nature of the curves of $W(t)$ for dinitrobenzene and trinitrobenzene; the higher the temperature, the less the relative maximum of the rate W_{\max}/W_0 and the earlier it occurs. Apparently, as is usually observed, the activation energy of a self-accelerating reaction is less than the primary energy, and correspondingly as the temperature is increased the specific share of the latter increases. This picture can, incidentally, be observed in sequential reactions as well, if the fate of the second stage depends more strongly on temperature than that of the first.

Mono-, Di- and Trichlorotrinitrobenzene

The decomposition of monochlorotrinitrobenzene in the vapor stage occurs under comparable conditions four times more rapidly than that of trinitrobenzene; the acceleration of gas formation is slightly less and also, although more weakly than trinitrobenzene, increases with increasing m/v ratio. The introduction of glass capillaries, as was observed for all the nitro-compounds studied in the vapor stage, strongly increases the rate of gas formation and changes the nature of the curve of $p(t)$.

The dependence of the rate of decomposition on temperature is considerably weaker than for trinitrobenzene; $k = 10^{8.45} \exp(-37,000 RT)$. Di- and trichlorotrinitrobenzene are similar in reaction rate (at 330°C , $P_0 = 150$ mm) to the monochloro-compound.

Trinitrotoluene

The decomposition of methyltrinitrobenzene—trinitrotoluene—was studied in the temperature interval $280\text{--}320^\circ\text{C}$ with an initial pressure of $70\text{--}200$ mm; this decomposition process occurs much (1000 times) more rapidly than that of trinitrobenzene; an acceleration is observed, although it is less (2–3 times according to the value of W_{max}/W_0) than that of trinitrobenzene. The initial rate, as well as the degree of acceleration increase (Figure 41) has the equivalent figures for trinitrobenzene as the m/v ratio is increased (initial vapor pressure P_0); at $P_0 = 40$ mm the rate (absolute) is almost constant with time; at $P_0 = 160$ mm, the initial rate is 3 times, the maximum rate 6 times greater than at 40 mm. As the m/v ratio is increased, the time required to reach the maximum is also decreased.

An increase in vessel surface (by 5 times) by introducing glass capillaries sharply (60 times) increases the initial rate of decomposition as was observed for trinitrobenzene; the rate in this case did not increase, but decreased with time; this decrease in rate (for the heterogeneous component) can be easily placed on a straight line following the first order reaction rule.

The construction of an Arrhenius dependent for the initial rate at constant initial pressure (80 mm) does not produce a straight line. A straight line is produced if at various temperatures the rate is taken with identical corrected pressures (P_0/P_s , where P_s is the trinitrotoluene vapor pressure at the given temperature. For ratios $P_0/P_s = 0.19\text{--}0.25$, the activation energy is

34.5 kcal/mol, and the factor before the exponent is $10^{8.45}$; at higher ratios P_0/P_s (0.41–0.46), these values are equal to 31.5 and $10^{7.4}$ respectively.

Trinitrophenol

Trinitrophenol in the vapor phase, like trinitrobenzene and trinitrotoluene, is decomposed at low pressures (30 mm) with slight acceleration and (at 290°C) twice as rapidly as trinitrotoluene. An increase in initial pressure increases both the initial rate and the maximum rate, particularly strongly when the vapor pressure approximates the pressure of the saturated vapor. The time required to reach the maximum is shortened. An increase of the surface by 10 times sharply (100 times) increases the initial decomposition (Figure 42); reaching a maximum, the pressure begins to decrease slowly, apparently as a result of the formation of condensed products.

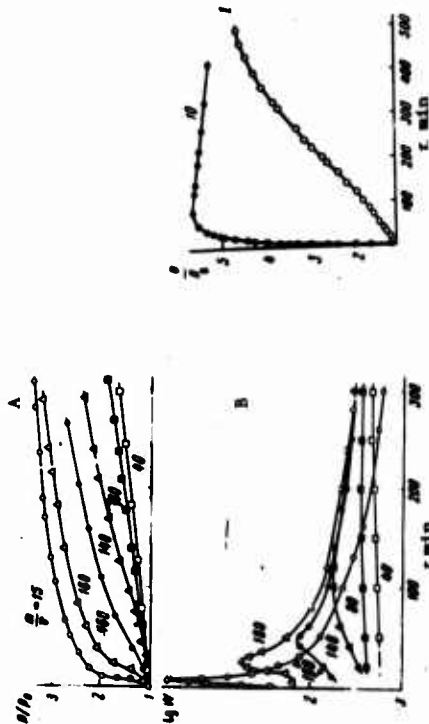


Figure 41. Influence of initial pressure on change in pressure (A) and rate of gas formation (B) with time in decomposition of trinitrotoluene. Numbers by curves indicate pressure (P_0 , mm Hg); 180 mm Hg is saturated vapor pressure; an experiment with index (m/v and $\text{g/cm}^3 \cdot 10^{-4}$)—figures are for mixture of vapor and liquid.

Figure 42. Decomposition of trinitrophenol in vapor phase at 290°C . Upper curve, relative surface of glass equal to 10, lower curve—1.

Trinitroaniline

Trinitroaniline is decomposed in the vapor phase at 300°C considerably more slowly than trinitrotoluene (by 20 times) and only twice as fast as trinitrobenzene. From the dependence of the initial rate on temperature ($E = 38.5$ kcal/mol and $\log B = 8.8$). The initial rate and rate maximum increase with pressure as is observed for other nitro-compounds described above. A similar influence (strong increase of initial rate, disappearance of acceleration stage) is achieved by packing the vessel with capillaries. The heterogeneous reaction occurs according to the first order reaction rule.

2. Decomposition of Nitro-Compounds in the Liquid Phase

Trinitrobenzene

The decomposition of liquid trinitrobenzene in the temperature interval 250-310°C occurs approximately 10 times as rapidly, with the same specific gas formation, but with greater acceleration, as the same process in the vapor phase.

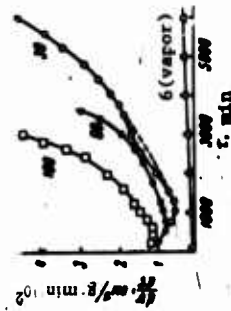


Figure 43. Decomposition of liquid trinitrobenzene at 271°C. Numbers indicate the complex nature of the conversion: by curves are m/v ratio ($\text{g/cm}^3 \cdot 10^{-4}$).

The form of the curves showing the change in rate of gas formation with time at low temperatures (Figure 43) indicate the complex nature of the conversion: the rate first decreases, then begins to increase. The increase in the m/v ratio, that is pressure of gaseous products at a certain stage of decomposition, slightly increases the rate of gas formation and more strongly increases its growth with time, as well as the rate maximum. It increases also regardless of

the increase in pressure as the process develops, and is shown by a comparison of values of the rate with the same pressure, but at different stages of decomposition. The influence of the m/v ratio also appears at higher temperatures (Figure 44). The self-acceleration of gas formation is apparently not a manifestation of autocatalysis, since the addition of partially decomposed products to fresh products does not lead to an increase in the rate above to the additive rate. The introduction of glass powder to the liquid does not accelerate gas formation, while glass capillaries above the liquid strongly increase the rate of gas formation. The dependence of the rate on temperature is determined in the initial (2-3% decomposition) sector at $m/v = 100 \cdot 10^{-4}$ g/cm^3 and follows the equation $k = 10^{10.9} \exp (-43,000/RT)$.

Tetranitrobenzene

The decomposition of liquid tetranitrobenzene occurs not only considerably more rapidly (at 220°C and $m/v = 100 \cdot 10^{-4}$ g/cm^3 , approximately 300 more times rapidly) than trinitrobenzene, but also is essentially different from the latter as concerns the nature of the curve of $p(t)$ and the influence of m/v on the decomposition rate.

For example, at 220°C, as well as at lower temperatures (Figure 45) decomposition occurs with high initial rate, although its increase with time is not observed; also, gas formation almost ceases after separation of a certain volume of gases (300 cm^3 at 220°C), which is considerably less than with complete decomposition of trinitrobenzene. Apparently, as tetranitrobenzene decomposes a stable intermediate product is formed which is capable of further decomposition with the formation of gases.

Another specific feature of the decomposition of tetranitrobenzene is the fact that its rate both at 220 and 180 and 140°C does not increase as the rate of decomposition of all other nitro-compounds in the benzene series does, but decreases essentially as the m/v ratio is increased (Figure 46). The reasons for this difference have not been established, although we can assume the formation of an intermediate product which decomposes reversibly with the formation of gases; the same picture would be produced if the decomposition occurred practically entirely in the vapor phase, the relative quantity of which is inversely proportional to the m/v ratio.

law $p = Ae^{kt}$. The acceleration constant increased with temperature $k = 10^{11.4} \exp(-34,400/RT)$, where k is expressed in inverse seconds.

Over the sector of retarded gas formation, its rate decreases according to the first order reaction rule, where $E = 34$ kcal/mol and $\log B = 11$. The activation energy calculated from the linear dependence of the logarithm of flash delay on the inverse of temperature is 32 kcal/mol.

Robertson also studied the influence of various additives to the decomposition of trinitrotoluene. Many of the additives in small quantities increase k and correspondingly decrease the delay of the ignition. None of the additives studied had a delaying effect.

According to Maksimov, decomposition of liquid trotyl at 290°C occurs, as in the case of the decomposition of trinitrobenzene, approximately 10 times more rapidly than in the vapor phase, with an acceleration which increases slightly as the m/v ratio is increased. A viscous, brown material which is soluble in acetone can be separated from the material half decomposed at 230°C; this brown material decomposes at the same temperature according to the first order rule at a rate tens of times higher than the rate of decomposition of trotyl itself (Figure 47). Addition of this material to trotyl in a quantity of only 3% divides the time required to reach the maximum rate by 3 (Figure 48). Since the experimental curve goes considerably higher than a simple additive curve, it should be concluded that the intermediate product has an accelerating, possibly catalytic effect on the decomposition of trotyl, which agrees with the observations of Robertson [64].

In order to determine the coefficients of the temperature dependence, the decomposition was traced at four temperatures (193, 210, 230 and 250°C) with m/v ratios at which the share of the condensed phase was identical (0.9). The curves produced (up to 25% P_{con}) as well as the time scale is changed. According to the Arrhenius straight line $E = 26.2$ kcal/mol.

Trinitrophenol

The principal experiments on the decomposition of liquid trinitrophenol were conducted at low values of m/v ($10 \cdot 10^{-4}$ g/cm³), allowing the entire course of decomposition to be followed. Decomposition in the liquid state occurs considerably more rapidly than in the vapor state, while the rate of decomposition of liquid trinitrophenol, extrapolated from 183-270° to 290°, is 10 times

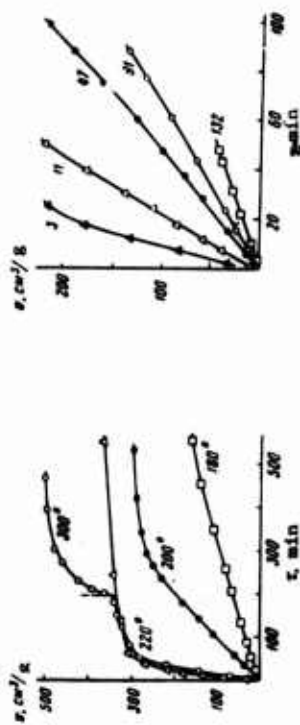


Figure 45. Decomposition of liquid tetranitrobenzene at various temperatures. Parallel experiment at 220°C was continued at 300°C.

Figure 46. Influence of m/v ratio on decomposition of tetranitrobenzene at 220°C. Numbers by curves— m/v (g/cm³ · 10⁻⁴).

Mono-, Di- and Trichlorotrinitrobenzene

The decomposition of mono-, di- and trichlorotrinitrobenzenes in liquid phase occurs with the rate 5-10 times greater than the rate in the vapor phase and considerably more rapidly than that of trinitrobenzene. Upon transition from mono- to trichlorosubstituted benzene, the rate of decomposition decreases. Under comparable conditions (250°C, $m/v = 100 \cdot 10^{-4}$ g/cm³) the rates for trinitrobenzene, monochlorotrinitrobenzene, dichlorotrinitrobenzene and trichlorotrinitrobenzene are related as 1:80:50:5. During the course of decomposition, the rate increases by 5-10 times.

Trinitrotoluene

Orginskiy et al [63] established that the thermal decomposition of trinitrotoluene in the 220-270°C temperature interval occurs with self-acceleration, which is preceded by a considerable induction period at low temperature. The acceleration is apparently a result of the accumulation of condensed autocatalyst, since, as the experiments of Yu. P. Zakharov have shown, evacuation of gases during decomposition does not lead to any noticeable change in the rate of gas formation. The higher the temperature, the greater the rate maximum and the more rapidly it is reached.

A. Robertson [64] confirmed the self-accelerating nature of the decomposition of trinitrotoluene—pressure increased with time according to an exponential

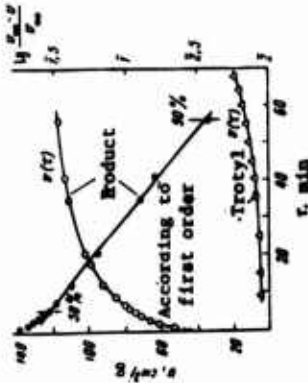


Figure 47. Decomposition of trotyl at 230°C and intermediate products separated from it. Test of course of decomposition of intermediate

products by first order, $\log \frac{p_{\infty}-p}{p_{\infty}} = -kt$

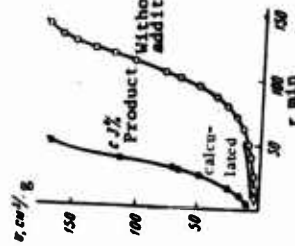


Figure 48. Influence of addition of 3% intermediate product to decomposition of trotyl at 230°C.

greater than in the vapor phase. The course of the decomposition curves (Figure 49) is unique and indicate the complex occurrence of decomposition, in which at least five stages can be distinguished, differing in the nature of the dependence of the rate of gas formation on time. As a whole, acceleration in the decomposition of trinitrophenol is expressed quite weakly, much less than in the decomposition of trotyl and other substituted trinitrobenzenes. The first stage, clearly observed at low temperatures (and high m/v values) is the induction period, followed by the second stage (II)—acceleration of gas formation; the third stage (III) is a reaction whose rate decreases with time, and the quantity of gases liberated by the end of this stage increases with temperature and at 180–270°C amounts to 5–20% of the total final quantity. The fourth stage (IV) is characterized by a considerably lower (by 3–9 times) rate of gas formation than the maximum rate in the third stage; the rate does not decrease, but rather increases, although weakly, with time. This increase is expressed more strongly, the lower the temperature. The rate increases with an increase in the m/v ratio. In the fifth stage (V) the rate decreases, apparently as a result of a decrease in the quantity of initial material. The activation energy can be calculated from the values of mean rate in the IV stage at various temperatures ($E = 38.5$ kcal/mol) and assuming first order reaction, the factor before the exponent can be calculated ($\log B = 11.7$).

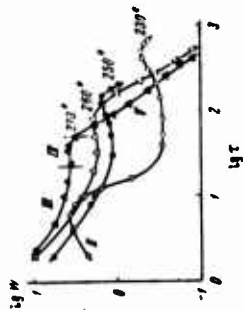


Figure 49. Change in rate of decomposition with time ($\log W - \log t$) in the decomposition of trinitrophenol at various temperatures. Roman numbers indicate individual decomposition stages.

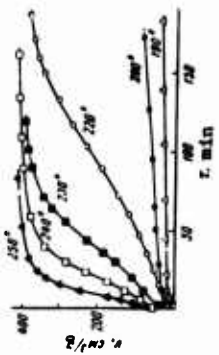


Figure 50. Decomposition of liquid trinitroresorcinol at various temperatures.

Trinitroresorcinol

The study of the thermal decomposition of trinitroresorcinol is hindered by the fact that it relatively firmly holds water. The rate of decomposition is considerably greater (approximately 10 times) than that of trinitrophenol. The total picture of the decomposition (Figure 50) is similar to that observed for trinitrophenol. The decomposition is accompanied by a slight initial increase in gas formation (first stage), decomposition with considerable but rapidly decreasing speed (second stage), a sector of slightly increasing speed (third stage) and, finally, a decrease once more. The first stage is found only in experiments performed at the lowest temperatures studied (180–200°C); this is partially true of the second stage as well, the duration of which was about 10 minutes at this temperature, while the quantity of gases adsorbed was 20–35 cm^3/g . The third stage—the slightly accelerating gas formation—covers the principal portion of the decomposition process; its rate is much less (6–8 times) than that of the preceding stage, and the increase in rate is slight as well; at 200°C, it is only 1.56, while at higher temperatures it is even less. The temperature dependence has been estimated the same as for trinitrophenol, and indicates $E = 34.6$ kcal/mol $\log B = 11.2$.

Trinitroaniline

Liquid trinitroaniline is decomposed significantly more rapidly than gaseous trinitroaniline: when data on the decomposition of vapors are extrapolated to

a temperature of 275°C, at which the liquid was studied, the rates differ by 15-20 times ($m/v = 30 \cdot 10^{-4} \text{ g/cm}^3$).

However, the rate of gas formation increases strongly as the m/v value is increased, so that at higher m/v values the difference between the liquid and the vapors is even greater. The rate of decomposition increases with time and at its maximum exceeds the initial value by approximately 10 times; at higher values of m/v , the acceleration of decomposition with time decreases and even ceases entirely (Figure 51).

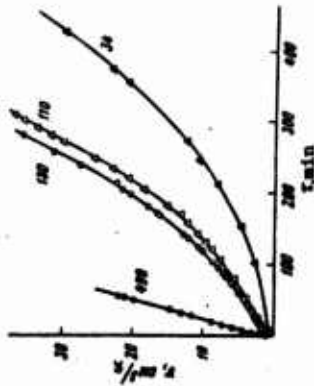


Figure 51. Decomposition of liquid trinitroaniline at 275°C and various values of m/v ratio. Numbers by curves are m/v ($\text{g/cm}^3 \cdot 10^{-4}$).

The dependence of the rate of gas formation on temperature was determined by matching curves of $v(t)$, produced at various temperatures and approximately identical ratios m/v ($100-150 \cdot 10^{-4} \text{ g/cm}^3$). The curves are satisfactorily matched only in their initial sectors (up to $p = 0.025 p_{\text{con}}$); Arrhenius calculation gives us $E = 31 \text{ kcal/mol}$ and $\log B = 7.1$.

Compounds with Two Benzene Rings

Liquid hexanitrodiphenyl decomposes with an acceleration (at 245°C $W_{\text{max}}/W_0 = 8$) (Figure 52) approximately the same as for nitrobenzene, but the initial rate (at 290°C) is 10-15 times greater than that of trinitrobenzene. The acceleration of gas formation increases with an increase in m/v ratio, more strongly, the lower the temperature. Determination of the dependence of rate on temperature was performed by matching of curves of $v(t)$ over the sector from the beginning of decomposition to achievement of $v = 0.13 v_{\text{con}}$, yielding $E = 49.5 \text{ kcal/mol}$ and $\log B = 16.1$.

Liquid hexanitrodiphenyl sulfide decomposes at 245°C 10 times more rapidly than hexanitrodiphenyl, that is 100 times more rapidly than trinitrobenzene. The decomposition occurs with considerable acceleration. At 235°C, the rate at its maximum is 10 times greater than the initial rate. The increase in temperature (at constant m/v) increases the W_{max}/W_0 ratio. A change in the m/v ratio only slightly influences the course of decomposition. Addition of partially decomposed material causes a considerable acceleration of decomposition.

At relatively low temperatures (235-255°C) with high m/v ($100 \cdot 10^{-4} \text{ g/cm}^3$) the decomposition has a clearly two-staged nature in its initial stages (Figure 53). Matching of curves for various temperatures (in the sector up to 6% decomposition) can be used to determine the dependence of gas formation rate on temperature, which gives us $E = 43 \text{ kcal/mol}$.

Liquid hexyl (m.p. 243°C) at relatively high temperature decomposes at a rate somewhat higher than trinitrophenol, which decreases with time. An increase in the m/v ratio decreases the total gas formation rate, particularly in the initial stage. At the lowest of the temperatures studied (250°C) in the initial stage of decomposition a slight acceleration is observed, similar to that established for trinitrophenol under similar conditions.

The course of the curve of $v(t)$ for hexanitrooxanilide (m.p. 332°C) at 338°C is similar (Figure 54). The "half decomposition time" is three times as great as for trinitrophenol, but 200 times less than for trinitrobenzene.

Decomposition at High m/v Ratios

All data analyzed above on the decomposition of nitro-compounds in the liquid phase were produced with m/v not over $500 \cdot 10^{-4} \text{ g/cm}^3$; this allowed us to trace the process of decomposition over a considerable time. Under the conditions of its application, decomposition might occur at considerably higher volume filling factors. In connection with this, the decomposition of certain explosives has also been studied at high m/v ($2000-6000 \cdot 10^{-4} \text{ g/cm}^3$). For trinitrobenzene, the initial rate of decomposition (250°C) as the value of m/v is increased from $330 \cdot 10^{-4}$ to $6500 \cdot 10^{-4} \text{ g/cm}^3$ continues to increase, but relatively weakly (in this interval of m/v , by only 1.3 times); the acceleration of decomposition increases somewhat more strongly.

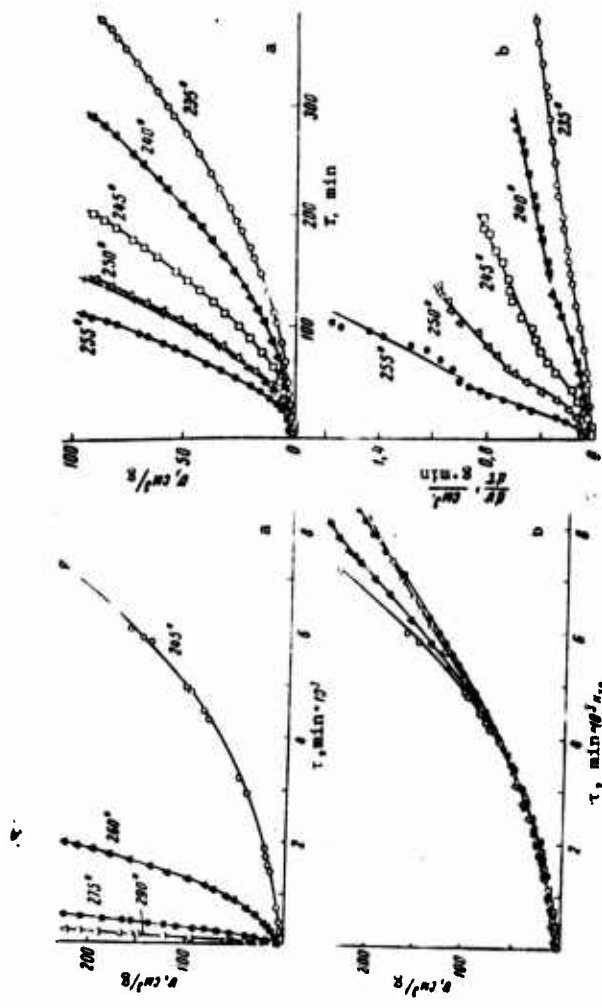


Figure 52. Decomposition of liquid hexanitrodiphenyl at various temperatures (a) and matching of v- τ curves with changed time scale (b) ($m/v = 10 \cdot 10^{-4}$ g/cm³, k_{tp} - transformation coefficient).

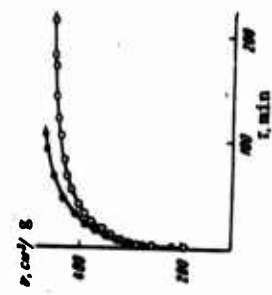


Figure 53. Decomposition of liquid hexanitrodiphenyl sulfide at various temperatures. a, change in pressure with time; b, change in rate of gas formation with time.

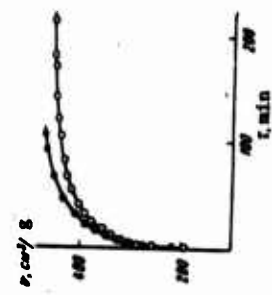


Figure 54. Decomposition of liquid hexanitrooxanilide at 338°C.

An increase in the m/v ratio has a similar influence on the decomposition of monochlorotrinitrobenzene: as it is increased from $40 \cdot 10^{-4}$ to $40,000 \cdot 10^{-4}$ g/cm³, the initial rate increases by only 3 times. The relative acceleration (W_{max}/W_0) is independent of m/v . For tetranitrobenzene (220°C) upon transition from $m/v = 3 \cdot 10^{-4}$ to $1750 \cdot 10^{-4}$ g/cm³, the rate of decomposition decreases by 50 times. Acceleration of decomposition with time is not observed for tetranitrobenzene either at low or at high values of m/v .

A more complex influence (increase in rate of gas formation in the early stages with an increase in the area of small values, followed by cessation of this increase at higher values of m/v) is observed in the decomposition of dichlorodinitrobenzene and trichlorotrinitrobenzene with varying m/v . However, we are concerned here with the liberation of very small quantities of gases, only a few cubic centimeters per gram, which might also be related to decomposition of possible impurities.

When the decomposition of explosives is compared to trinitrobenzene, the order of stability remains the same as with small m/v , but the quantitative distinctions are considerably less; thus, monochlorotrinitrobenzene is no longer 80 times less stable, but only 5 times less stable than trinitrobenzene.

3. Decomposition of Polynitro-Compounds in the Solid State

The introduction of certain substituents to the molecule of trinitrobenzene greatly increases the melting point; the same is observed for compounds containing two or more trinitrobenzene rings. The increase in the melting point may be so great that the rate of thermal decomposition becomes accessible to measurement below the melting point.

The rate of decomposition of explosives in the solid state, as is true for all other materials investigated in this respect, is considerably less than in the liquid state. Due to this, it seemed possible, by introducing substituents to trinitrobenzene which increase the melting point, or by producing polynitro-compounds with multiple rings, to increase the thermal stability. However, investigations have shown that the introduction of any substituent to trinitrobenzene increases the rate of decomposition, and that this increase predominates at all temperatures over the decrease in the rate resulting from the change in the state of the material. Thus, this means for increasing the thermal stability can have practical significance only if the material must be in the solid state

(we recall that trinitrobenzene is a relatively low melting material—m.p. 122°C); one reason for this requirement might be the great density of the solid material as compared to the melted material.

The decomposition of polynitro-compounds such as hexanitrodiphenyl, hexanitrodiphenyl sulfide, hexanitrodiphenyloxide, hexanitrodiphenylamine, hexanitroxanilide, diamino trinitrobenzene and triaminotrinitrobenzene in the solid state was studied by Maksimov.

Hexanitrodiphenyl melts at a relatively low temperature (240°C) at which its decomposition rate is quite low—1 g of the material in a 15 day period liberated only 15 cm³ of gas. At 216 and 231°C, the initial rates of gas formation were $2.7 \cdot 10^{-6}$ and $9.75 \cdot 10^{-6}$ cm³/gsec, which is approximately 10 times less than that indicated by extrapolation of the rate of gas formation of liquid hexanitrodiphenyl to these temperatures.

The volatile impurities contained in unpurified hexanitrodiphenyl significantly accelerate its decomposition both in the liquid and particularly in the solid state.

The decomposition of solid hexanitrodiphenyl sulfide (m.p. 233°C) was studied at 200–220°C. The acceleration of decomposition W_{\max}/W_0 is great and equal to 100 or 200° and 70 for 220°, which is almost 10 times greater than in the decomposition of the melted material and apparently is related to progressive melting of the material during the course of decomposition. The rate of gas formation increases slightly as the m/v value is increased. The onset of rapid acceleration of decomposition occurs much earlier with smaller crystals, but the rate in this last stage is greater for larger crystals. The rate of decomposition of the solid material is 3–5 times less than that of the liquid material. For the solid material, calculation using the temperature dependents of the integral curve transformation factor gives us $E = 42,70$ kcal/mol.

The decomposition of hexanitrodiphenyloxide (m.p. 266°C) in the solid state occurs with an acceleration of 10. The rate during the acceleration stage increases exponentially. The higher the purity of the product (evaluated by m.p.) the less the rate of decomposition.

Hexanitrodiphenylamine (m.p. 242°C) decomposes relatively rapidly in the solid state as well, but with a rate which decreases with time. It increases with temperature relatively slowly—in the sector of relative constancy the

rate $k_{10} = 1.8$, while for the melted material at higher temperatures $k \approx 3$. The content of compounds which condense at room temperature in the gaseous decomposition products increases considerably as decomposition continues.

The decomposition of hexanitroxanilide (m.p. 332°C) in the liquid state (at 338°C), which occurs with a decrease in rate with time, compares to its decomposition below the melting point, which occurs differently depending on m/v. An increase of m/v ratio has a dual influence—the rate of gas formation decreases, while the acceleration increases. Quantitatively, both of these influences depend also on the temperature of the experiment (Figure 55). Matching of initial sectors of the integral curves for the solid material gives us $E = 51.5$ kcal/mol, $\log B = 16.0$. The rate of gas formation decreases somewhat with increasing crystal size.

The decomposition of diaminotrinitrobenzene (m.p. 289°C) is accompanied by partial liquification, greater, the higher the decomposition temperature. The rate-time curves show two rate maxima, more sharply expressed, the higher the experimental temperature (Figure 56). The first of these begins after 2–5% of the total quantity of gases have been separated, the second—after about 50%. At lower temperatures, the nature of the curves changes essentially. A change in crystal size by a factor of 10 has no significant influence on the nature and rate of gas formation.

The decomposition of triaminotrinitrobenzene (decomposes without melting in melting point determination) depends only weakly on m/v and on crystal size. In the interval 284–320°C, decomposition occurs (Figure 57) with relatively slight (2.5–2.9) acceleration, the value of which is independent of temperature; the rate maximum occurs relatively late, at 50–80% decomposition. The integral curves match well to the completion of decomposition, which gives us $E = 41.8$ kcal/mol, $\log B = 11.56$.

IV. N-Nitramines

The decomposition of aliphatic nitromines has been investigated for methylenedinitramine and ethylenedinitramine.

Methylenedinitramine ($\text{Medina } \text{NO}_2\text{HN}-\text{CH}_2-\text{NHNO}_2$)

The decomposition of medina (m.p. 105–106° with decomposition) was studied [65] by the method of continuous (by Westfal balance) or periodic determination of weight loss upon heating in open containers, in order to prevent the

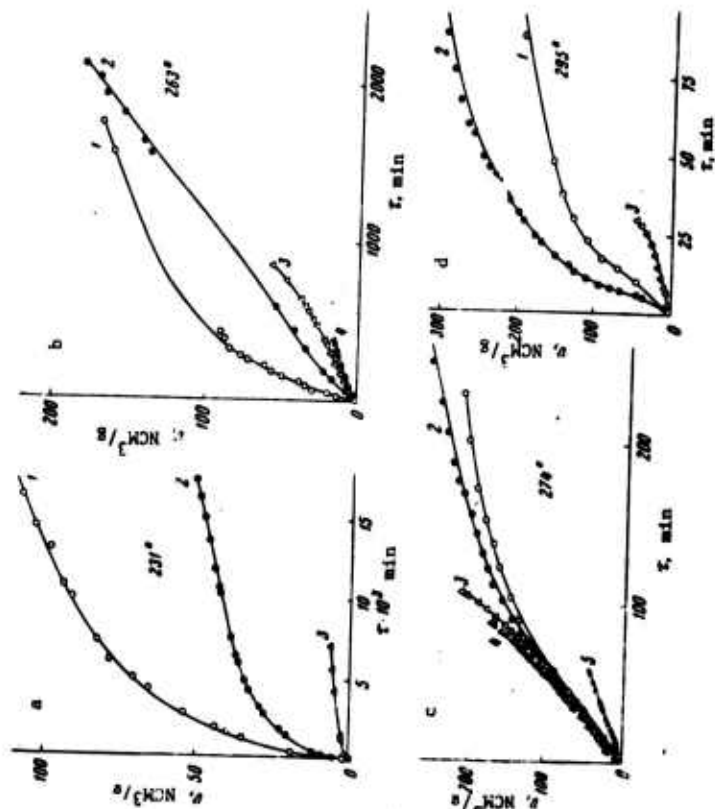


Figure 55. Decomposition of solid hexanitrooxanilide at various temperatures and m/v ratios ($\text{g}/\text{cm}^3 \cdot 10^{-4}$): a: 1, 10; 2, 75; 3, 303. b: 1, 2; 2, 10; 3, 82; 4, 264. c: 1, 10; 2, 10; 3, 60; 4, 100; 5, 270. d: 1, 10, 2, 18; 3, 86.

accumulation of volatile products which might accelerate the process. The final weight loss was about 45%; the residue was a white powder, insoluble in water, benzene, acetone and alcohol, decomposing at $\sim 208^\circ\text{C}$.

Decomposition of the melt in the temperature interval $110\text{--}130^\circ\text{C}$ occurs without an acceleration at a rate proportional to the quantity of undecomposed material remaining. Its constant is $k = 10^{15.6} \exp(-35,400/\text{RT})$.

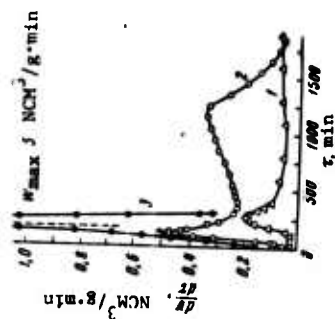


Figure 56. Change in rate of decomposition of solid diamotrinobenzene with time at $m/v = 10 \cdot 10^{-4} \text{ g}/\text{cm}^3$ and various temperatures ($^\circ\text{C}$): 1, 259; 2, 269; 3, 279.

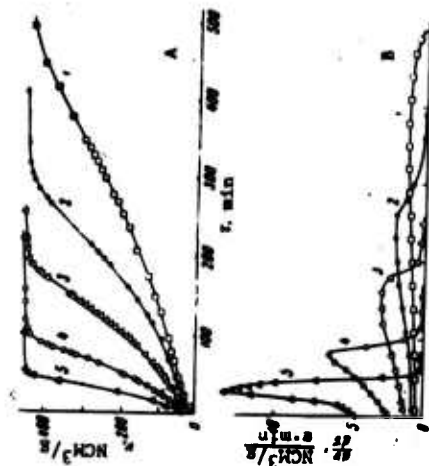


Figure 57. Change in gas formation (A) and rate of gas formation (B) during decomposition of trinitrotrinitrobenzene at $m/v = 10 \cdot 10^{-4} \text{ g}/\text{cm}^3$ at various temperatures ($^\circ\text{C}$): 1, 284; 2, 293; 3, 305; 4, 311; 5, 320.

The decomposition of the solid material at 70-100°C begins with an induction period, during which about 1% of the material is decomposed and the rate drops. This is followed by a period of acceleration. The addition of picric acid to the solution with subsequent removal of the solvent has no influence on the length of the induction period and the development of the subsequent acceleration; however, the quantity of material decomposed in the induction period is decreased, showing the inhibiting effect of picric acid. This effect, it is assumed by the authors of the investigation, is related to prevention of the surface reaction of seed formation, since the picric acid was introduced in such a way that it was located only on the surface of the particles of the material. The similarity in the nature of decomposition with that observed for solid, non-melting salts, allows us to assume that it is topochemical, related with the formation of seeds on the surface of the crystals and subsequent seed growth. However, the fact that the experimental temperature was near the melting point of the initial material, and the complete melting of medina observed in other experiments when decomposition was performed near the melting point indicates the possibility of another acceleration mechanism--progressive transition of the solid material to melted material as a result of the accumulation of soluble decomposition products within it. The rate of decomposition of melted medina, as would be expected, is much greater than that of solid medina.

Ethylenedinitramine (EDNA, $\text{NO}_2\text{FN}-\text{CH}_2\text{CH}_2-\text{NHNO}_2$)

Thermal decomposition of ethylenedinitramine (m.p. 176.5°C, dried over sulfuric acid, purity 99.95%) was studied at temperatures below the melting point (60-120°C) and above it (180-254°C), as well as in aqueous solutions [66,64].

When dry EDNA was decomposed in a vacuum (initial pressure 2-5 mm, powder fraction between screens with openings of 0.147-0.295 mm) curve p-r at 100°C as, at least at first, a saturated nature; at 120°C the rate is approximately constant for 50 hr, then increases exponentially over the sector to 2-3% decomposition.

At 1 atm and 120°C, an induction period of 100-150 hr is observed, followed by exponential increase of the rate continuing to 25% decomposition; in a 50% mixture with trotyl, the exponential acceleration is observed throughout the entire decomposition process.

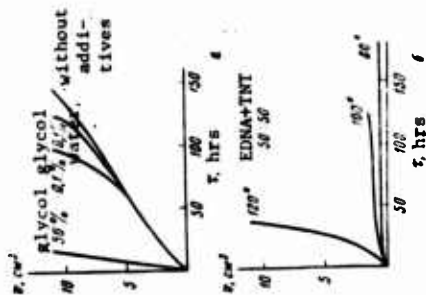


Figure 58. Influence of various impurities (a) and trotyl (TNT) (b) on decomposition of EDNA.

Admixtures of water (0.1%) or glycol (0.1 and particularly 50%) accelerate decomposition; the mixture with trotyl (50:50) also decomposes considerably more rapidly than EDNA itself (Figure 58). The gaseous decomposition products do not accelerate decomposition; it seems, without concrete data, that an increase in charge size or specific surface accelerates decomposition. In contrast to what should occur according to the Arrhenius formula, the temperature coefficient of the reaction rate does not decrease, but rather increases as temperature increases: the effective value of activation energy increases from 36-37 kcal/mol at 100-120° to 51.5 kcal/mol at 135-145°C.

At high temperatures [64] in a vacuum (10^{-3} mm) the material was evaporated and condensed onto cold portions of the apparatus, before noticeable decomposition had occurred. In order to prevent evaporation, an inert gas, usually nitrogen was used, under a pressure of 10 cm. Under these conditions, the liquid explosive was decomposed in the temperature interval 184-254°C with a rate proportional to the quantity of undecomposed material remaining. The time to half decomposition was 43 sec at 184° and one-half sec at 254°C. The rate constant at low temperatures did not depend on the quantity of material; this indicates the homogeneity of the decomposition reaction. For kinetic experiments at higher temperatures, in order to avoid ignition and provide rapid heating, very small charges had to be used.

The rate constant $k = 10^{12.8} \exp (-30,500/RT)$.

The gaseous decomposition end products at 195°C were present in the following quantities per mole of material: NO, 0.10; N₂O, 1.4; N₂, 0.39; CO, 0.028 and CO₂, 0.065. Water and acetaldehyde were also formed.

In aqueous solutions, EDNA decomposes with hydrolysis, forming nitrous oxide, ethylene glycol and acetaldehyde. The rate of hydrolysis is rather great, then increases with increasing acidity (H₂SO₄) of the solution and temperature; with time, it decreases according to the first order reaction rule; thus, autocatalytic acceleration of hydrolysis is not observed. Transition from a neutral solution to 0.009 N increases the rate constant by almost 2.5 times, while in 0.5 N acid it is 127 times faster than in the neutral solution.

The reason for the acceleration of decomposition of solid EDNA with time must be considered the accumulation of condensed decomposition products. However, their effect is not necessarily catalytic in the general sense of this word. This is indicated by the absence of acceleration in the decomposition of melted EDNA in the experiments of Robertson [64]; however, these experiments were performed at relatively high temperatures, when the role of autocatalysis may be relatively slight; therefore, it would be more convincing to observe absence of self-acceleration in the decomposition of solutions of EDNA in an inert solvent, for example trotyl, at relatively low (100-120°C) temperatures. The most probable reason for the acceleration is transition of an increasing portion of EDNA to the liquid state as a result of the accumulation of condensed decomposition products, due to the mutual solubility of the initial material and the products of its decomposition. The rate of decomposition of liquid EDNA is much greater than that of solid EDNA. The accelerating influence of trotyl, in which EDNA is markedly soluble, should also be explained in the same manner. This explanation of the acceleration of the decomposition is more probably than that related with the development of topochemical acceleration of decomposition in the solid phase. The exponential increase in the rate with time observed in the decomposition of the solid product cannot be considered a sufficient basis to state, as Tomlinson did [66], that the decomposition is a chain process. The fulfillment of this dependence in the presence of trotyl is additional evidence in favor of the explanation of the acceleration of decomposition by liquification of the initial material.

Trinitrophenylmethylnitramine [Tetryl, C₆H₂(NO₂)₃NCH₂NO₂]

Tetryl is decomposed at a considerable rate at its melting point (131.5°C); therefore, its decomposition can be studied at temperatures either above or below the melting point [67].

In order to establish the order of the reaction, the rate of decomposition of melted tetryl and its solutions in trotyl were determined (Table 6). The trotyl was used as a solvent since in this temperature interval it remains practically undecomposed and at the same time is resistant to those chemically active products which might be formed in the decomposition of tetryl.

Table 6

Rate of Decomposition of Tetryl as a Function of its Concentration

Time, hours	Moles of gas per 1 mole of tetryl		
	Pure tetryl	33% tetryl solution	16.6% tetryl solution
1	0.18	0.23	0.19
2	0.49	0.63	0.54
3	0.86	1.00	0.84
4	1.19	1.28	1.09
5	1.46	1.50	1.30
6	1.64	1.65	1.43

The results of these experiments show that the rate is not dependent on concentration of tetryl, which indicates that the main reaction in the decomposition process is monomolecular.

However, in its initial stages the decomposition does include acceleration. This shows that, in addition to the monomolecular reaction, an autocatalytic reaction also occurs. The autocatalyst presumed active is the picric acid formed in the reaction.

With the simple assumption that the acceleration of the reaction by the catalyst is proportional to the first power of its concentration, we can obtain the following expression for the summary rate

$$\frac{1}{t} \ln \frac{a}{a-x} + \frac{1}{t} \ln \left(1 + \frac{x}{a} \right) = \text{const} = S, \quad (2.28)$$

where $k = k_1/k_2$ is the ratio of the constants of the monomolecular and autocatalytic reactions.

The data of two measurements made at 140°C were used to calculate the value of the constant $k = 0.187$. Knowing this value, we can test the constancy of constant S throughout the entire experiment, that is the correctness of the autocatalytic reaction equation for the decomposition of tetryl. The calculations show good constancy of the constant, which varies within limits not exceeding 1%.

The experiments in which picric acid was added to the tetryl also quantitatively confirmed the assumption of its catalyzing effect, apparently related to the effects of the hydrogen ion.

The catalyzing effect of picric acid on the thermal decomposition of tetryl has been confirmed also in the work of Roginskiy et al [68] by the ignition delay method.

A charge of tetryl (0.3 g) was placed in a glass ampule with a capacity of 2.5 cm³; the ampule was sealed, placed in a thermostat and the time to ignition was determined. At 156°C, the addition of 5% picric acid reduced the time to ignition from 29 min to 21 min, while 20% reduced the time to 13.5 min. A further increase in the picric acid did not decrease the time to ignition; apparently, its diluting effect came into play.

It was shown in this same work that, in addition to the formation of picric acid, the ignition of tetryl is influenced by the experimental conditions. It was established that in open ampules under certain experimental conditions ignition did not occur at 150-170°C. In sealed ampules ignition did occur, beginning at 150°C, and under these conditions the higher the quantity of material per unit volume of the ampule, that is the greater the gas pressure developed during decomposition, the lower the temperature at which ignition would occur¹⁰. This influence of "charging density" is observed for many explosives and Roginskiy feels that it is most naturally explained by assuming that the gaseous intermediate composition products have a strong influence on the rate of the reaction and the process of ignition. The concentration of these products in the liquid phase is obviously proportional to their pressure over the liquid.

¹⁰ See p. 131.

This explanation, however, has been contradicted by the direct experiments of R. Yu. Suslova for tetryl, who established that evacuation of the gaseous decomposition product or replacement with nitrogen has practically no influence on the rate of slow thermal decomposition of tetryl at 140°C.

Other explanations of the influence of the m/v ratio on the formation of ignition are possible.

For example, at high m/v values, the ampule may be broken not by ignition of the explosive, but simply by the pressure arising as a result of slow decomposition, which may become sufficient to break the ampule. It is understandable with no explanation that in this case the higher m/v, the more rapidly the pressure necessary to burst the ampule will be reached.

If an experiment is performed with values of m/v for which the maximum pressure of isothermal decomposition is insufficient to burst the ampule, increased m/v values and, consequently, increased gas pressures during decomposition may favor the formation of an explosion since the volume of gas bubbles formed in decomposition, which mix the liquid and thereby increase heat transfer¹¹, will be smaller. Further, the higher the m/v, the less the volume of free space over the liquid and the less the portion of the material which can be converted to the vapor phase; correspondingly, a greater portion of the material will remain in the liquid phase, and the conditions for the formation of a thermal explosion will be more favorable. Finally, it is possible that ignition can occur in a closed ampule in the explosive vapors according to the thermal mechanism, that is if the pressure (density) of the vapors exceeds the critical pressure, the maximum vapor density depends on the m/v ratio.

We could explain which of these possible influences of pressure is the most important by studying the ignition of explosive vapors without the liquid, as well as the formation of ignition under conditions excluding the formation of significant concentrations of explosive vapors.

The rate of decomposition of solid tetryl is 50-100 times less than the rate of decomposition of the liquid, calculated for the same temperature, but increases rapidly as the decomposition continues. The increase in the rate can be quantitatively explained by progressive transition of the solid tetryl during

¹¹ See p. 131.

the course of decomposition to the liquid state, as a result of the reduction in its melting point by the condensed decomposition product. This phenomenon is apparently general in nature and was observed for all explosives studied in this respect: the rate of decomposition in the solid state is considerably lower than in the melted state or in solution, but increases strongly with time for this reason.

The addition of nitric or acetic acids does not accelerate decomposition, probably due to the volatility of these acids; sulfuric acid does cause rapid liberation of gases.

The temperature coefficient of the rate is great--about 4 per 10°C at $120-150^{\circ}\text{C}$. This value of temperature coefficient leads to high activation energy and high preexponential factor in the decomposition reaction rate constant formula.

According to the calculations of Roginsky, $E = 60$ kcal/mol, while $B = 10^{27.5}$. True, a later work [64] performed at higher temperatures ($211-260^{\circ}\text{C}$) indicated $k = 10^{15.4} \exp(-38,000/RT)$, that is the value of B is only slightly greater than the usual value for monomolecular reactions. This problem requires further clarification.



Figure 59. Influence of degree of filling of vessel on decomposition of tetryl at 150° at various m/v ratios ($\text{g}/\text{cm}^3 \cdot 10^{-4}$): 1, 353.5; 2, 49.4; 3, 55; 4, 8.0; 5, 0 (with evacuation); η , depth of conversion.

Merzhanov et al [69] studied the decomposition of tetryl over a considerably greater interval of values of m/v (44 times greater). The experiments were performed in a stainless steel vessel, and the final pressure with the highest m/v value was 6,000 mm. A change in the charge size (by a factor of 7 at 150°C) had no influence on the course of decomposition.

The curves illustrating the degree of decomposition as a function of time (Figure 59) show that the degree of filling has a relatively weak influence on the rate. As the m/v ratio is increased from $8 \cdot 10^{-4}$ to $353.5 \cdot 10^{-4}$, the time to half decomposition is decreased only slightly. The difference in the rate of gas formation was even weaker, since less gas is formed at higher pressures.

In addition to the determination of pressure-time curves, the change in the composition of gaseous products was determined during the course of certain experiments at 150°C . This determination showed that at first the gases contained considerable quantities of NO_2 and N_2^1 , while during the further course of decomposition the quantity of NO_2 passed through a maximum and decreased considerably more rapidly than the quantity of NO . At lower m/v values, the maximum for both gases is less and arrives later.

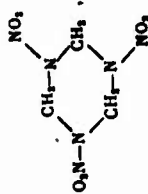
The change in the rates with time when the gaseous products are removed is described by the expression for first order autocatalyst. An attempt to consider the influence of gaseous products in a similar manner, assuming that they catalyze the decomposition and that this effect is proportional to their pressure over the liquid, that is the concentration in it, was unsuccessful. This is not surprising: the presence of such reactive gases as the oxides of nitrogen in the reaction products, and the variations in their concentration during the course of the process clearly indicate that it includes successive reactions with the participation of the gaseous products, occurring with the formation of gases. The decrease in the rate when the gases are evacuated and the gradual increase in rate as the experiment continues together with the accumulation of NO_2 in the decomposition products confirm these considerations. There is no reason therefore to analyze the influence of the gaseous decomposition products as a catalytic effect of the end products as was done for the condensed decomposition products--picric acid--by Hinschelwood. Let us add that the relationship between the gaseous compounds of nitrogen and carbon produced in this work

¹² See p. 132.

differ essentially from that which would be expected from the conversion of trinitrophenylethylamine to trinitrophenol: the number of gram/atoms of nitrogen was 3 times greater than that of carbon.

Hexogen and Octogen

The decomposition of melted hexogen, cyclotrimethylene trinitramine



was studied by Robertson [70] at 213-299°C in rather small charges in order to assure that decomposition would occur without an ignition. Throughout this temperature interval, the decomposition occurs according to the first order reaction rule¹³ with a half decomposition time of 410 sec at 213 and 0.25 sec at 299°C. The reaction rate does not change in the presence of air, nitrogen or hydrogen at various pressures right up to atmospheric pressure or when the material contacts the surface of mica or copper.

The dependence of the rate constant on temperature is expressed by the Arrhenius relationship with $E = 47.5$ kcal/mol and $\log B = 18.5$.

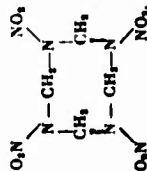
Experiments with dilute (2 and 5%) solutions of hexogen in dicyclohexylphthalate and trotyl at over 250°C show the monomolecular nature of the reaction. The low 250°C, self-acceleration of the reaction occurs, judging from the linear initial sector of the curve. This self-acceleration is expressed more strongly the lower the temperature and at 200°C a linear dependence is observed until pressures is reached amounting to half the final pressure, after which the first order reaction equation is followed. The presence of autocatalysis is also indicated by the results of an experiment in which a solvent from a preceding experiment was used; the rate was considerably higher. This indicates in particular that the catalyst is a rather stable compound in relation to the hexogen itself.

¹³ See p. 132.

For 2% and 5% solutions of hexogen, the rate constants were calculated using the initial sector of the line considering the final pressure. For cyclohexylphthalate solutions, $E = 41.0$ kcal/mol, $\log B = 15.46$. The decomposition rate in trotyl solutions is slightly lower.

A comparison of the rates for the melt and for solutions shows that in the latter case the rate of decomposition is less; the difference is very slight at 200°C, increasing with temperature.

The decomposition of octogen, cyclotetramethylene tetranitramine,



occurs more slowly than that of hexogen; it was studied in a medium of hydrogen or air under a pressure of 5 cm. In experiments at over 280°C, the material melted rapidly and decomposed monomolecularly in liquid form. The half decomposition period was 16 sec at 271 and 0.45 sec at 314°C. For hexogen, calculations indicate a time of 0.015 sec at this temperature, i.e. 30 times faster.

Analysis of the gaseous decomposition products of hexogen (with an initial nitrogen pressure of 6 cm) as well as those of octogen gave the results presented in Table 7.

In addition to the gases indicated in the table, considerable quantities of water and formaldehyde are formed, as well as a solid residue.

We can see from the table that the composition of the decomposition products changes with temperature; this indicates the complex nature of the reaction. The gas composition changes noticeably also upon transition from melted to dissolved hexogen and depends on the solvent used.

Maksimov studied the thermal decomposition of hexogen by a manometric method, after purifying his product by recrystallization from acetone (m.p. 202.8-203.0°C) in solid form (at 150-197°C) with m/v from $3.6 \cdot 10^{-4}$ to $1870 \cdot 10^{-4}$ g/cm³. The rate of gas formation increases with time, reaching at its maximum 5-20 times the initial value¹⁴. The rate is strongly dependent on the m/v ratio,

¹⁴ See p. 132.

Table 7

Gaseous Products of Decomposition of Hexogen and Octogen
(in moles per mole of explosive) Under Various Experimental Conditions

Temperature, °C	Decomposition Products					
	NO	N ₂ O	N ₂	H ₂	CO	CO ₂
Hexogen						
257	0.75	0.76	1.03	0.06	0.29	0.44
225	0.54	0.98	1.16	0.09	0.40	0.48
Hexogen as 5% solution in dicyclohexylphthalate						
225	0.15	1.13	0.89	0.45	0.16	0.33
Hexogen as 5% solution in trotyl						
264	1.02	0.47	1.33	0.30	0.32	0.85
220	0.70	0.63	1.83	0.20	0.57	0.83
Octogen (after decomposition for 2 min)						
280	0.95	1.51	1.16	—	0.57	0.64

decreasing, in contrast to many other explosives, as it increases (Figure 60). The maximum of the rate occurs later, the greater the value m/v . Increasing m/v increases the ratio of the maximum rate to the initial rate.

A change in crystal dimensions by 10-20 times has practically no influence on the rate of decomposition; when the crystals were placed beneath a layer of inert (silicon) liquid, the rate decreased slightly.

At considerable m/v ($100 \cdot 10^{-4} \text{ g/cm}^3$) the increase in speed with time may be expressed by the relationship $W = k_1 e^{k_2 t}$, where k_1 and k_2 increase with temperature. Thus, the rate of gas formation increases proportionally to the quantity of decomposition products formed.

In the initial sectors, up to about 1% decomposition, the curves of $v(t)$ can be matched, and this matching occurs at $E = 51.0 \text{ kcal/mol}$ and $\log B = 18.6$.

The addition of small quantities of trotyl (Figure 61) has a dual influence on the decomposition. At first, gas formation is greater than when the trotyl is absent, but delayed in time; later, an acceleration of gas formation is noted. The first increase in rate may be related to liquification of a portion of the hexogen as a result of its solution in the liquid trotyl. This explanation is favored by the fact that the initial rate in the presence of trotyl increases more rapidly with temperature.

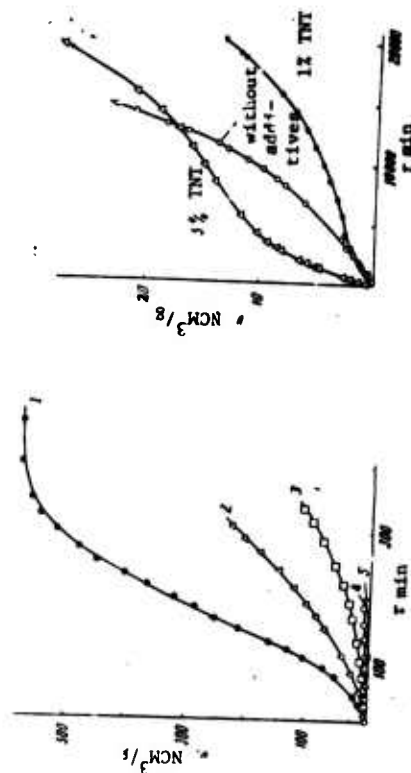


Figure 60. Thermal decomposition of hexogen at 190°C at various degrees of filling of the vessel with material. Values of m/v ratio ($\text{g/cm}^3 \cdot 10^{-4}$): 1, 3.6; 2, 11; 3, 101; 4, 540; 5, 1870.

Figure 61. Influence of small quantities of trotyl on decomposition of hexogen at 150°C and $m/v = 10 \cdot 10^{-4} \text{ g/cm}^3$.

The decomposition of hexogen dissolved in dinitrobenzene was studied in this same temperature interval. The decomposition (Figure 62) occurs more rapidly than that of the solid material (at 180°C, 16 times more rapidly) but with less acceleration, although acceleration increases with increasing temperature (Figure 63). The rate at the maximum exceeds the initial rate by 2-5 times. This observation contradicts the data of Robertson presented above, who observed a decrease in acceleration with increasing temperature, although this was in a higher temperature range (above 250°C).

An increase in the concentration of hexogen from 4 to 15% has practically no influence on its decomposition; during the stage of decreasing decomposition rate, it changes in correspondence with the first order reaction equation. During the course of decomposition, the color of the solution changes from weak green to dark cerise.

The temperature dependence, determined by the matching of curves in the sector up to liberation of 30% of the gases, gives us a value of activation energy of 41.3 kcal/mol and $\log B = 15.3$.

The rate constant at 200°C is $1.5 \cdot 10^{-4} \text{ sec}^{-1}$, which is one half that produced by Robertson in a dicyclohexylphthalate solution. The rate of decomposition

of dissolved hexogen depends less on temperature than that of solid hexogen; therefore, at low temperatures the difference between them as concerns the rate of decomposition increases.

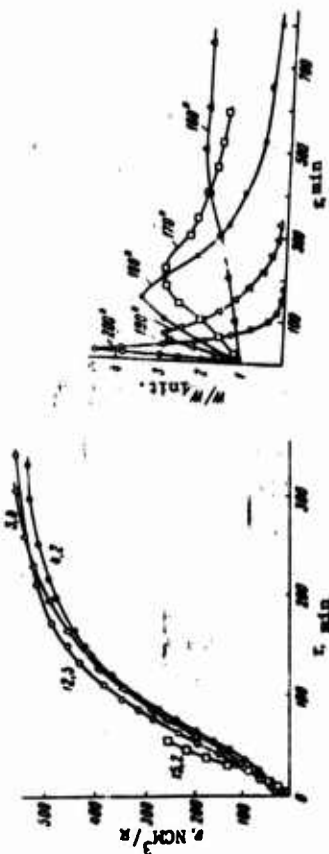


Figure 62. Decomposition of hexogen dissolved in dinitrobenzene at 190°C. Numbers by curves indicate weight concentration of hexogen in percent.

The decomposition of octogen (m.p. 272.5°C) in the solid state (176-230°C) at m/v ratios of $5 \cdot 10^{-4}$ - $500 \cdot 10^{-4}$ g/cm³ occurs with more acceleration than that of hexogen. At 150°C, the initial rate of decomposition of octogen is the same as that of hexogen; at higher temperatures, the oxygen is decomposed more slowly. As in the case for hexogen, the rate of gas formation at low m/v values is greater than at higher values, but beginning with $m/v = 10 \cdot 10^{-4}$ g/cm³, does not change with further increases in m/v . The ratio of the rate at the maximum to the initial rate at $m/v = 5 \cdot 10^{-4}$ g/cm³ is 8; as m/v is increased, it increases so that, beginning at a certain degree of decomposition, the rate of gas formation at high m/v values is greater than at lower values.

Large grained octogen decomposes somewhat more rapidly than fine grained octogen. Beginning at 1X decomposition and up to 20%, the change in the rate during the course of the decomposition can be expressed by the exponential dependence $W = k \cdot t^n$, where the exponent n is independent of temperature and is equal to 1.3-1.4, while the constant k increases with temperature. The matching of curves of $v(t)$ over the sector up to formation of 10 cm^3 of gases per 1 g (complete decomposition yields $600 \text{ cm}^3/\text{g}$) for the temperature interval 180-230°C leads to $E = 36.5 \text{ kcal/mol}$ and $\log B = 10.7$.

The decomposition of octogen was also studied for its solution in dinitrobenzene (171-215°C, octogen content from 0.5 to 2%); its rate is 8 times greater than that of solid octogen. A change in the concentration has almost no influence on the rate of gas formation or the change of this rate with time. At first the decomposition occurs as is observed for hexogen, with slight acceleration, increasing like the degree of decomposition at the maximum with increasing temperature.

The curves of $v(t)$ match well up to 1/3 decomposition. The values calculated by curve matching are $E = 42.6 \text{ kcal/mol}$, $\log B = 14.9$. A comparison of the results produced for solutions of octogen and hexogen shows that at 150-200°, octogen decomposes more slowly than hexogen.

V. Hydrazoic Acid (HN_3)

Hydrazoic acid is a very sensitive and dangerous explosive liquid, boiling at 37°C. Therefore, its decomposition has been studied only in the gaseous state [72]. Experiments have been performed in quartz and glass vessels in the temperature interval 306-330°C at pressures of 30-200 mm. The decomposition of HN_3 leads almost quantitatively to the formation of ammonia, according to the equation



The rate of the reaction becomes measurable at temperatures over 250°C. The reaction occurs primarily on the walls of the vessel. It generally follows the monomolecular law; the half decomposition period at 330° in a glass vessel is about 12 min. Slight impurities strongly catalyze the decomposition and easily lead to explosions. The reaction rate is strongly dependent on the surface. An increase in the ratio of surface to volume by 8 times increases the reaction rate by approximately 5 times. In quartz vessels the reaction occurred 3 times more slowly than in glass vessels. The value of the rate constant fluctuated strongly, which did not allow the activation energy to be calculated. An increase in temperature by 10° lead to an increase in the rate by 1.5-2 times in a glass vessel; addition of inert gases (He , H_2 and N) has no influence. It must be noted that an explosive so sensitive as hydrazoic acid does have relatively high thermal stability.

VI. Explosives Which Decompose in the Solid State

In the preceding sections, we have analyzed the decomposition of explosives which (with the exception of nitrocellulose) could be in the liquid state at the experimental temperature. Many explosives (primarily heavy metal salts) have melting points above their flash point. For others, the melting point is rather high, and they decompose at considerable rates below this temperature in the solid state.

As we know, autocatalytic decomposition of solids can be reduced to two cases of decomposition: topochemical and chain decomposition. Topochemical decomposition in turn occurs differently with respect to the dependence of the reaction rate and quantity of reacted material on time with a small and constant number of seeds on the one hand, and with a large number on the other hand.

An example of topochemical decomposition (first case) might be the decomposition of calcium azide (CaN_6).

During a manometric investigation of the decomposition of this material [8] at 100-140°C, S-shaped curves were produced, showing the change in the pressure of nitrogen formed during decomposition with time (Figure 64). The decomposition process can be divided into three stages:

- 1) an induction period with very low and practically constant rate (AB);
- 2) a sharp increase in decomposition rate (BC);
- 3) a decrease in rate (CD).

The induction period in the decomposition of calcium azide apparently results to considerable extent from the influence of impurities which destroy the reaction seeds and prevent the development of the reaction. When these impurities are exhausted, seeds can grow, and the reaction rate begins to increase rapidly.

This explanation is supported on the one hand by the great variability of the duration of the induction period and on the other hand by experiments on decomposition conducted in an atmosphere of water vapor or oxygen. In the presence of these two gases, the reaction rate is almost equal to zero, while evaporation of the gases causes a sharp increase in the rate, in contrast to the slow development of the process observed at the beginning of decomposition of a fresh specimen.

During the period of acceleration, the reaction rate follows the topochemical

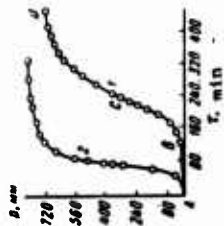


Figure 64. Thermal decomposition of calcium azide in a vacuum. 1, under a layer of paraffin; 2, without paraffin.

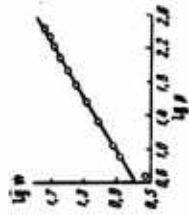


Figure 65. Rate of decomposition of calcium azide as a function of quantity of material decomposed.

rule rather well for the case where the rate of formation of seeds is equal to zero: $dx/dt = kx^{2/3}$. This latter condition was achieved by preliminary heating of the azide at a higher temperature until the end of the induction period was approached. Then the temperature was dropped and decomposition performed at this lower temperature, at which practically no new seeds were formed, while seed growth continued¹⁵ for the seeds which had already been formed. The fulfillment of this equation can be particularly clearly seen by constructing a graph of $\log W$ vs. $\log P$, which should produce a straight line with a tangent of the angle of inclination of $2/3$. A straight line is actually produced, and $\tan \alpha = 0.65$ (Figure 65).

In the last stage, the decrease in rate mathematically follows the monomolecular law as is observed for other solid explosives.

A calculation of the activation energy showed that in the interval 80-100°C it is equal to 20 kcal/mol. It is interesting that as the temperature is increased the activation energy does not remain constant, but grows, reaching 34,000 cal/mol at 140°C.

An investigation of the decomposition of calcium azide revealed that the introduction of paraffin to a test tube containing the azide so that the azide was covered by a layer of paraffin leads to a sharp slowdown of the decomposition (see Figure 64, curve 1). The induction period becomes three times as long, the transition to acceleration is not as sharp, and the rate during the subsequent course of the reaction is significantly less. The decelerating influence of paraffin is also evident if it is introduced after the reaction has

¹⁵ See p. 132.

already begun: the rate immediately becomes 40 times less. A similar influence of paraffin was established later for the decomposition of silver oxalate [73] and for thermal decomposition of nickel formate [74].

The mechanism of the action of the paraffin is not quite clear. The most probable reason for the deceleration of the reaction is deactivation by the paraffin of some intermediate reaction product which accelerates the process. This influence is apparently general in nature and can be used as a criterion for the establishment of the topochemical nature of a reaction. In this connection, it is useful to recall the phlegmatizing influence of paraffin and similar liquids as concerns the sensitivity of explosives to shock. It is possible that the similarity of the effects of paraffin in both cases is not by chance.

Garner and Reeves [75] studied the influence of ultraviolet radiation on the subsequent thermal decomposition of calcium azide. Irradiation greatly decreases the induction period and increases the decomposition rate. The exponential law of rate increase is retained.

Another example of topochemical decomposition is the decomposition of silver oxalate [76]. The course of the decomposition is illustrated by curves similar to the curves for calcium azide. The quantity of reacted material increases proportionally to t^m , where $m = 3.5^{16}$. Preliminary drying, a change in separation conditions and grinding influence the decomposition rate. However, differences in the rate are less than those which are sometimes observed between identically prepared and processed specimens of oxalate. Irradiation of silver oxalate before decomposition by light with a wave length of less than 520 mμ greatly increases the rate of subsequent thermal reaction. Contacts with oxygen during irradiation noticeably decreases the influence of irradiation in comparison with to irradiation in an atmosphere of nitrogen, carbon dioxide or in a vacuum. An increase in the quantity of reacted materials for small irradiation periods is noted, approximately proportional to the number of quanta absorbed, while for longer irradiation times it is less.

Many other explosives and nonexplosive materials decompose according to the same type of decomposition as calcium azide and silver oxalate--fulminate of mercury [77], silver oxide [78], barium azide [75], and strontium azide [75].

16 See p. 132.

Together with the investigation of the decomposition of crystalline powders, these materials were investigated in the form of individual large crystals (in order to avoid the complicating influence resulting from differences in dimensions and properties of individual crystals). Such a crystal, weighing 0.5-5 mg, was placed in a platinum boat suspended on a thin wire and lowered by a special device into a vessel carefully evacuated at the experimental temperature. The change in pressure, amounting to a few tenths of a millimeter, was measured by a MacLeod or Pirani manometer.

The external appearance of decomposition for the various explosives studied is as follows: for fulminative mercury $[Hg(ONC)_2]$ at 100-115°C, first a very rapid, slight yield of gas is observed, which Garner first attributed to liberation of gases adsorbed on the external and internal surfaces of the crystal and the surface of the platinum boat. The investigations of Apin [79] into the decomposition of lead azide showed, however, that actually the increase in pressure is related to the first superficial reaction. This can be clearly seen from the curve showing the rate as a function of time (Figure 66); after the maximum, the rate decreases sharply and only after a certain time does a new rate increase begin, resulting from a reaction occurring in the case of the decomposition of the azide throughout the entire mass of the crystal. The reality of both maxima is confirmed also by measurements of self-heating during the reaction. Similar dual maxima on the rate curve are observed for the decomposition of other solid explosive and nonexplosive materials.



Figure 66. Thermal decomposition of lead azide (charge of 0.1000 g).

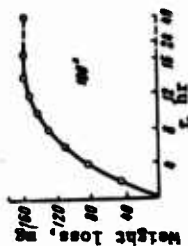


Figure 67. Thermal decomposition of trinitrotriazidobenzene.

After the initial acceleration, the reaction of decomposition of fulminative mercury enters an induction period, during which the rate of gas liberation is quite low, the pressure increasing linearly with time. At the same time, the crystal becomes brown. At the end of the induction period, the crystal breaks up, most of the fragments being yellow in color. This acceleration is primarily superficial.

At the end of the induction period, the reaction accelerates. This acceleration continues until the gas pressure over the crystal reaches $1/3-2/3$ of its final value, after which for a certain period of time the reaction rate remains constant. At the end of the acceleration period, the entire crystal becomes brown, although most of the fulminative mercury has not yet decomposed. During the subsequent stage, the reaction rate is proportional to the quantity of undecomposed material, that is is expressed by the first order reaction equation $k = (1/t) \cdot \ln(a/a - x)$, which continues to be followed until the end of the decomposition. If the crystal is fragmented, the induction period decreases greatly; if it is ground, it is practically absent, but otherwise the general course of the decomposition remains unchanged.

This same type of decomposition is observed for lead azide if small crystals are used. The acceleration is observed until approximately one half of the material has been decomposed.

Crystals of barium azide ($\text{BaN}_6 \cdot \text{H}_2\text{O}$) [80] lose their water of crystallization even at room temperature, forming a white pseudomorphous mass. The dehydrated crystals, following the induction period, are decomposed with measurable speed at temperatures above 95°C , and seeds, the number of which increases with time, and which can be seen under the microscope, arise both on the external and on the internal surfaces of the crystal, have irregular form and are grouped on the surface in bunches. The general course of the decomposition is qualitatively the same as for fulminative mercury, but the pressure during the acceleration sector increases in proportion to the sixth power of time.

The case when the number of seeds is great [81] and the reaction products rapidly cover the surface of the crystal, according to Garner, is observed when the azides of lead¹⁷ and silver are decomposed [82]. Apparently, it also occurs in the decomposition of trinitrotriazidobenzene into hexanitrobenzene and nitrogen [83] at low temperatures (100° and lower) which occurs according

¹⁷ See p. 132.

to the equation



The dependence between the quantity of reacted material and the time is illustrated by the curve on Figure 67. Analysis of this curve has shown [84] that decomposition follows the following rule quite closely:

$$a^{1/3} - (a - x)^{1/3} = \frac{1}{3} kt.$$

A comparison of the values of decomposition rate constants at various temperatures ($70-100^\circ\text{C}$) indicates decomposition activation energies for solid trinitrotriazidobenzene of 32, 300 cal/mol.

Turek [85] studied the decomposition of trinitromonazidobenzene, trinitrodiazidobenzene and trinitrotriazidobenzene in the solid state at 50° and in the form of 1% solutions in carbon tetrachloride at 61 and 76.5°C by the liberation of nitrogen. According to the data for solutions, in which decomposition occurs without noticeable acceleration, the activation energies are similar and amount to 22,400, 25,300 and 23,800 cal/mol. It is interesting to note that the decomposition rate is highest of all for trinitromonazidobenzene and least of all for trinitrotriazidobenzene. These rates differ by 7 times in solution at 76.5° and by 5 times in the solid state at 50°C . All three materials decompose considerably more rapidly in solution than in the solid state.

The decomposition of trinitrodiazidobenzene at 50°C occurs with acceleration; according to the experiments with Ioffe [96] the decomposition of solid trinitrotriazidobenzene occurs in exactly the same way at elevated temperatures. This acceleration should be explained by a gradual transition of the solid material to liquid as a result of a decrease in the melting point by the decomposition products. We add that Ioffe's experiments indicate that the rate of decomposition is also influenced by the pressure under which decomposition occurs; the rate of decomposition is greater, the higher the pressure.

One characteristic feature for the topochemical process is the presence of an acceleration sector over which the rate increases exponentially with time, as a result of the growth of three-dimensional seeds of the reaction.

For certain solid materials (both explosive and nonexplosive) a considerable acceleration period is also observed, but the rate in this period increases not logarithmically but exponentially¹⁸

¹⁸ See p. 132.

$$\frac{dx}{dt} = A e^{at}$$

As an example, we can cite the decomposition of trinitroresorcinate of lead [87] $[C_6H(NO_2)_3O_2Pb \cdot H_2O]$ (Figure 68). When this material is heated in a vacuum to 120°C first of all the water of crystallization is lost, although this dehydration does not result in a change of the form or transparency of the crystal. At temperatures over 200°C, the water crystallization is lost very rapidly and the crystal breaks into sections. The dehydration is followed by thermal decomposition, and if the temperature is over 225°C, it ends in explosion. The curves for the acceleration sector were similar in observations of the oxalates of several heavy metals and permanganates.

Thermal decomposition of the picrates and styphnates of ammonium, potassium and lead in the temperature interval 190–300° was studied by L. Yu. Rao-fen [88]. The change in pressure of gaseous decomposition products was used to establish the course of the decomposition with time at various temperatures, the influence of the pressure of the gaseous products on decomposition was studied by changing the degree of filling of the vessel, and the rate dependence was studied as a function of temperature.

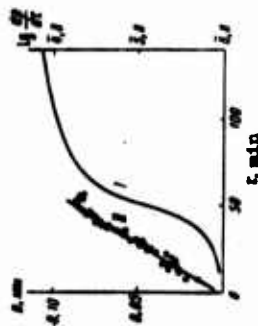


Figure 68. Thermal decomposition of lead trinitroresorcinate. I, $p = f(t)$; II, $\log dp/dt = f(t)$.

For all salts, the absolute rate of gas formation increases with time over a significant share of the decomposition. The decrease in rate, resulting from a decrease in the concentration (and in this case the quantity) of reagents occurs relatively late.

The initial rate of decomposition of all salts studied was less than that of the corresponding acids. However, since the rate of decomposition of salts increases more rapidly with temperature and with time, the maximum rate in many cases is higher for the salts than for the acids.

A third peculiarity is the staged nature for many salts, clearly visible even on integral curves. The principal type of staged effect is the combination of two acceleration stages, like those observed in the decomposition of ammonium styphnate (Table 8), but with considerable variations both in the amount of acceleration and the share of gas formation involved in each of these stages (the steepness of the transition from one stage to the next), as well as in the relative time which they occupy. As a rule, acceleration is stronger in the first stage than in the second. In some cases at the beginning of decomposition there is an induction period which is more (potassium picrate and disubstituted styphnate) or less (monosubstituted potassium styphnate) sharply expressed.

Table 8 shows a general representation of the nature of curves of v/t for the salts studied, as well as for the initial acids, and certain quantitative characteristics of the rate of decomposition, expressed through the period required to reach the pressure equal to $1/2$ of the maximum pressure.


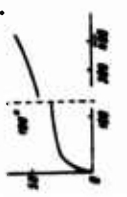

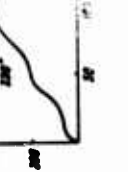
Due to the complex nature of the v/t curves, it is not possible to describe them with a simple mathematical expression; however, over more or less extended sectors, the curves can be described by various semiempirical relationships, in particular a power or exponential formula (Table 9). Sometimes, in order to produce a straight line in these coordinates it is necessary to discount the initial values of rate or volume of gaseous products.

As a rule, the acceleration of gas formation is relatively greater at low temperatures¹⁹. Thus for ammonium picrate at 230°C the maximum rate exceeds the initial rate by 18 times, while at 270°C it exceeds the initial rate by only 5.5 times. Throughout the entire temperature interval acceleration is considerably greater than for the corresponding acids. The differences in acceleration in many cases cause the curves for gas formation vs. time to intersect for salts and acids.

¹⁹ See p. 133.

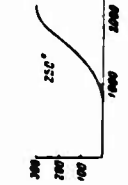

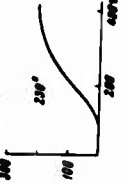
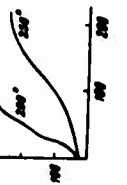

The dependence of decomposition rate on temperature was defined by various means: by initial rate, by comparison of $v-t$ curves (the curves for potassium picrate match particularly well), by comparison of mean values of rate using the constants of equations defining the dependence of rate on time, etc. (see Table 9). The rate in the second stage of decomposition depends less on temperature than that of the first stage. As a rule, the rate of decomposition of salts depends more strongly on temperature than that of acids (an exception is lead styphnate, for which the activation energy practically corresponds to the activation energy above the acid). The activation energies of disubstituted potassium styphnate and lead picrate are particularly great (about 60 kcal/mol).

Table 8
Principle Characteristics of Thermal Decomposition of Picric and Styphnic Acids and Their Salts

Material	Temperature interval (°C) and state	Nature of Decomposition	Time to half decomposition at 230°C, min	K_1^*	K_2^{**}
Picric acid	183-270 (liquid)		470	1	—
Styphnic acid	180-250 (liquid)		45	—	1
Ammonium picrate	200-270 (solid)		720	1.53	—
Ammonium styphnate	190-230 (solid)		65	—	1.44

(continued)

Table 8 (continued)

Material	Temperature interval (°C) and state	Nature of Decomposition	Time to half decomposition at 230°C, min	K_1^*	K_2^{**}
Potassium picrate	250-300 (solid)		8600	18.3	—
Monosubstituted potassium styphnate	170-200 (solid)		262±** (flash at 200°)	—	5.83
Disubstituted potassium styphnate	200-240 (solid)		210 (flash at 250°)	—	4.87
Lead picrate	230-260 (solid)		920 (flash at 260°)	1.96	—
Lead styphnate	200-230 (solid)		143 (explosion at 240°)	—	3.18

* K_1 is the ratio of the half decay periods of picrates and picric acid.
 ** K_2 is the ratio of the half decay periods of styphnates and styphnic acid.
 *** Determined by calculation.

Table 9

Activation Energy (E) of Thermal Decomposition of Picric and Styphnic Acids and Their Salts

Material	At a temperature interval, °C	E, kcal/mol	Method of Calculation of E
Picric acid	183-270	38.6	From mean values of rate at 5-50% decomposition
Potassium picrate	250-300	41.2	By matching of $v = f(\tau)$ curves
Ammonium picrate	200-270	43.0 40.5	By mean rate in decomposition of 3-11 to 45% (first value) and by tangent of angle of line $\log(v - v_0) = -A + k\tau$
Lead picrate	230-260	60.2 58.7	By tangent of angle of line $\log W = A + k\tau$ (first value) and mean rate at 10-50% decomposition
Styphnic acid	180-250	34.6	Values of mean rates at 22-45% decomposition
Monosubstituted potassium styphosphate	170-200	47.6	Values of rates at 5-35% decomposition
Disubstituted potassium styphosphate	200-240	51.7 52.9	Tangents of angle of lines $\log v = A + k\tau$ at 5-27% decomposition (first value) and mean rate in acceleration stage
Ammonium styphosphate	190-230	45.5 45.5	Mean rate in decomposition of 2-9 to 45% (first value) and angle of lines $\log W = A + k\tau$
Lead styphosphate	200-230	34.8 36.4	Values of rates at ~30% decomposition (first value) and angle of lines $\log v = A + k\tau$

'Since the rates do not differ strongly in absolute value throughout the temperature interval studied, the factor before the exponent is great for materials with strong temperature dependence of the rate and small, approaching the normal level, for materials whose rate of decomposition changes weakly with temperature.

The degree of filling the vessel with material (m/v), which determines the pressure of the gaseous decomposition products, has some influence, although generally not a strong influence, on the course of decomposition; the rate and the increase in rate with time both increase²⁰; as the m/v value increases, the rate of gas formation in the second stage also increases.

Szabo and Szava [89] studied the thermal decomposition of sodium picrate in an evacuated vessel, determining the delay in the flash τ (or time required to reach maximum rate) in the 300-310°C temperature interval, which lies between 1 and 13 minutes and was rather well reproducible. (The charge and its size and position were not indicated in this work.) The dependence $\tau(T)$ was used to calculate the activation energy ($E_\tau = 73$ kcal/mol) and the factor before the exponent ($\log B = 5$). The curves of $W(t)$ show the rate maximum during the first 0.5 min, which is not eliminated by drying or heating to 300° at atmospheric pressure, but decreases after treatment in a vacuum at 270°C. The pressure increases with time exponentially according to $W = Ae^{\phi t}$, and the activation energy, calculated by the temperature dependence of ϕ , was 65 kcal/mol.

For finely ground picrate, the induction period is 4-5 minutes shorter, while E_τ is considerably higher (93 kcal/mol), $E_\phi = 68$ kcal/mol.

Picrate produced by crystallization with an excess of potassium carbonate is decomposed and explodes considerably more rapidly than without this impurity; also, the dependence of τ on temperature becomes stronger, and partial preliminary decomposition at a slightly lower temperature retards flash formation when the temperature is subsequently raised; an excess of potassium picrate during crystallization does not have this influence.

The influence of various gases on the induction period was studied at 310°.

Under the influence of oxygen pressure (up to 300 mm) the induction period is decreased, while at $P_{O_2} = 600$ mm it increases to its previous value; with CO_2 pressure, on the other hand, the induction period increases at 300 mm and returns to its previous value by 600 mm, while nitrogen increases, throughout the entire pressure interval studied (up to 600 mm), hydrogen delays and hinders the flash point even more strongly. Evacuation of gases decomposition products does not change the induction period.

20 See p. 133.

Aging of the picrate (up to 1.5 years) at room temperature has no influence on the kinetics of its decomposition; at high (120, 150, 170 and 210°C) temperatures, 15 hours heating reduces the induction period and decreases the activation energy; the higher the aging temperature, the more stable this results; at 120°C, the after effects of aging disappear after one day.

Analysis of the results of investigation of the decomposition of solid explosives which accelerate exponentially was performed by Semenov [90]; he showed good agreement between the results produced and the chain plan of development of the reaction. This plan allows the presence and length of the induction period to be quantitatively explained, as well as the formation of visible seeds in some explosives and the absence of such seeds in others, the influence of grinding, the dependence of the time to explosion on temperature, etc.

We should mention at this point only the induction period, since its mechanism in this case is apparently different from the mechanism which we assumed for the topochemical decomposition of calcium azide and the autocatalytic decomposition of triethyl borate. In the latter two cases, the induction period results from the presence of impurities which retard the autocatalytic reaction. In the chain decomposition, however, Semenov considers the induction period to be apparent, produced as a result of slow development of the chain. In this case at first, when the pressure is very low and cannot be measured with the instruments used, the impression is given that there is no reaction. Actually, the reaction is taking place, accelerating according to the same rule from the very beginning right up to the end of the acceleration period, the difference being that we begin to notice it only after the pressure of the gases formed reaches a certain value. One confirmation of this point of view is the fact that the product of the induction period times ϕ always retains a constant value, as chain theory requires.

VII. Ammonium Perchlorate

We will not mention here the early investigations of the thermal decomposition of ammonium perchlorate, which have been covered in the review works [82, 91, 92], but will limit ourselves to analysis of a number of more recent works published primarily by foreign investigators.

The thermal decomposition of ammonium perchlorate, studied by Bircumshaw and Newman [93, 94], occurs quite uniquely. It would be expected that it would occur as follows: solid material \rightarrow gas. Actually, in most cases studied, the decomposition was as follows: solid material A \rightarrow solid material B + gas. In a high vacuum or in a current of inert gas at temperatures below 290°C, decomposition was stopped after the weight loss reached 30%. The residue after decomposition, which consisted of a crystal isomorphous to the initial salt but porous²¹ was completely composed of ammonium perchlorate.

The composition of the decomposition products below 300°C can be expressed by the equation



Above 350°C, the composition of the products corresponds more closely to the following equation, differing from the preceding equation in that nitric oxide is formed in place of nitrous oxide:



Also, hydrochloric and perchloric acids and nitrosyl chloride were formed.

The nature of propagation of the reaction through the perchlorate crystal, observed under the microscope for individual tiny crystals in various decomposition stages, clearly indicate its topochemical nature—discrete, nontransparent seeds are formed, which grow, merge and form an envelope of the product, surrounded by undecomposed material.

In most kinetic experiments, the decomposition was performed in an evacuated vessel, and the rate of gas formation at 250–300°C was determined by the increase in pressure of the constant gases (Mac-Leod) when the pumps were shut down briefly; the remaining gases were condensed in liquid oxygen; at 400°C and higher, slight nitrogen pressure was used (1–4 cm), in order to suppress sublimation, and the course of the decomposition was judged from the increase in pressure of the constant gases²².

The p(t) curves were S-shaped in nature; also, a slight induction period was noted, the length of which depended on the temperature and history of each specimen. The sector of decreasing rate was always greater than the acceleration sector; the time required to reach the maximum rate decreased with

²¹• ²² See p. 133.

increasing temperature; at 380-450°C, the curves corresponded almost completely to decreasing rate. Deuterated perchlorate decomposed somewhat more rapidly than ordinary perchlorate.

The assumption of the chemical poisoning of the reacting surface as a result of adsorption of gaseous decomposition products as a reason for the cessation of conversion was not confirmed. Possibly, a certain lattice configuration is necessary for the decomposition reaction to compete with sublimation.

The undecomposed perchlorate residue was completely decomposed at over 400°C, and the initial perchlorate also decomposed completely at this temperature. This indicates that the mechanism of decomposition differs in the two temperature intervals.

Galwey and Jacobs [95], considering that the dimensions of the particles making up the residue are the same as the dimensions of the elements in the mosaic structure of a crystal, assume that the 30% low temperature decomposition is the decomposition of the stressed material making up the elements of the mosaic; high temperature decomposition encompasses these elements themselves as well.

Water vapor and other solvents had a "rejuvenating" effect on the residue from decomposition, and during subsequent heating the decomposition continued. The degree of "rejuvenation" was proportional to the solubility of perchlorate in the solvent and the exposure time.

At 240°C, ammonium perchlorate undergoes a transition from the orthorhombic form to the cubic form, which has a notable influence on the rate maximum. We can see from Figure 69 that the maximum increases up to 238°, then decreases up to 250°C and once more begins increasing. The induction period decreases monotonously with temperature.

Experiments were also performed under nitrogen pressure (3 cm) at 260-300°C (using a quartz balance); these experiments produced results similar to those produced in the evacuated vessel. The increase in pressure due to the formation of noncondensing gases was about 2 mm. Further increase in the pressure of the inert gas changes the nature of the curve (weight loss-time); this influence is most strongly apparent as an increase in the rate of conversion during the stage in which, without the inert gas, it becomes near zero. The almost complete cessation of decomposition after conversion of 30% was not observed at high inert gas pressures.

The influence in an interruption in decomposition²³ (10 min) was studied. Below 240°C, it had no influence on the rate of subsequent decomposition.

Above 240°C, the rate always became greater than before the interruption, presumably because of the cracking of the crystals during the modification transition which occurred during cooling. In the acceleration sector, the rate increased by 2-3 times after the interruption, but then rapidly decreased.

At temperatures not far from the transition point--up to 255°C--the rate curve after the interruption had two maxima and one minimum. This is explained by the nearness to the transition temperature and by the fact that the sample was not immediately heated to the required temperature after the experiment was resumed; cracking during cooling caused the first maximum; the new transition to the cubic form once more led to formation of fresh surface, which yielded the second maximum. The degree of decomposition in these experiments did not exceed 28-30%.

Also, the influence of certain impurities, in particular ammonium nitrate, which might be an intermediate product, was studied. The presence of nitrate slightly decreased the induction period (from 30 to 15 min at 230°C). Perchloric acid which, like H-ions, was detected among the decomposition products, also leads to a shortening of the induction period, although the maximum rate was not as great as in the presence of ammonium nitrate.

The influence of ammonia was studied on the basis of the following considerations. If the first stage was decomposition of perchlorate to perchloric acid and ammonia, the latter would increase the induction period; this was observed during experiments. The induction period of ammonium perchlorate recrystallized from an aqueous ammonia solution was increased to 50 min, while the rate of subsequent decomposition was much slower, although its ordinary limit--28%--was not exceeded. Ammonia vapors also have a delaying effect. When the sample was heated for 2 hours at an NH_3 pressure of 3.5 cm (230°C), the degree of decomposition was reduced from ~30% to 3%.

We know that ammonium chloride strongly accelerates the thermal decomposition of ammonium nitrate. Its addition to perchlorate, however, had a reverse effect: the induction period at 230°C was increased by 10 min.

²³ See p. 133.

Curves of $p(t)$ were analyzed on the basis of the Prout-Thompkin's equation for the acceleration sector

$$\lg \frac{p}{p_{\infty} - p} = k_1 t + C_1 \quad (2.34)$$

with various values of the constant for periods of acceleration and decrease in speed; the acceleration period (up to $x \approx 0.25$) can also be described by the logarithmic expression $p = kt^n$ where $n \approx 6$.

For the period of decrease in speed, the first order reaction equation was used

$$-\lg (p_{\infty} - p) = k_2 t + C_2 \quad (2.35)$$

For the increase in speed with the Prout-Thompkin's formula in Arrhenious coordinates, straight lines are produced both for orthorhombic and cubic forms. The lines for the sector of decreasing speed show a clear break at the transition temperature, but are not straight lines. Calculation of the activation energy was also performed using the formula $\tau = \frac{E}{RT} = \text{const}$, where τ is the time of decomposition of a definite portion of the material (0.1 or 0.5) and gave results similar to those produced using the logarithmic expression.

The data produced for the activation energy are presented in Table 11. Due to the complexity of the decomposition process, the physical sense of this quantity in this case is not quite clear.

Table 11

Values of Activation Energy

Formulas Used	Activation Energy, kcal/mol	
	<240°C	>240°C
Acceleration sector on curve of $p(t) \lg \tau = \frac{E}{RT} + C$ $\tau = t_{0.5}$ $\tau = t_{0.1}$	28.4	18.4
	28.8	17.1
	24.9	23.0
$\lg \left(\frac{p}{p_{\infty} - p} \right) = k_1 t + C_1$		
Sector of decreasing speed on curve of $\lg (p_{\infty} - p) = k_2 t + C_2$ (first order)	28.8	20.5
	27.7	17.5
Mean values	27.8	18.9

The influence of particle size on the rate of decomposition was studied at 230° [100].

The salt was crushed and screened into fractions, and the influence of particle size was determined from the curves of the rate and its various constants. The maximum rate climbs rapidly as particle size decreases to a certain limit, then decreases. The reproducibility of results with sharply fractionated composition was less; also, the distribution of charges in the vessel had an influence: if a charge was distributed over a considerable length of the tube, the rate was less than if the charge was concentrated at the end of the tube. With equal particle sizes perchlorate produced by grinding large crystals decomposes more rapidly than if the small particles are produced by rapid crystallization. When particles of different sizes are produced by screening crystalline perchlorate without preliminary grinding, the rate of decomposition of the different fractions is almost the same, probably since the large particles are agglomerates of smaller crystals.

Galwey and Jacobs [101] studied the decomposition of ammonium perchlorate in the form of whole crystals, ground powder and (775 atm) tablets.

The methods of these experiments consisted of heating of a sample in a vacuum with measurement of the volume of gases formed by two Mac-Leod manometers for various pressure intervals. In the experiments with tablets at above 240°C measurement of the total pressure of all gases using a glass spiral manometer was used.

It was found in particular that various processing steps influence the behavior of the residue after decomposition when it is subsequently used for experiments. Shaking to break up large chunks, holding in air for 20 minutes, two days storage in a vacuum gave no essential rejuvenation; on the other hand, after grinding with subsequent seven day storage, the perchlorate was rejuvenated almost completely.

The Prout-Thompkin's equation, which was used by Bircumshaw, et al, is usually used to describe a quasi-chain acceleration process; in this case, the formation and growth of three dimensional seeds is observed. Also, this equation does not give a good description of the course of the decomposition²⁴

²⁴ See p. 133.

particularly for crystals and powder. Therefore, Galvey and Jacobs used the Avrami-Yerofeyev equation, representing it in the form $\ln(1 - \alpha) \sim t^4$ for the initial stage and $\ln(1 - \alpha) \sim t^3$ for the final stage of decomposition. These equations describe decomposition over a considerable length of time quite well. Thus, for whole crystals $n = 4$ in the interval $\alpha = 0.02-0.20$ and $n = 3$ for $\alpha = 0.20-0.90$; the corresponding values of E are 20.6 and 16.9 kcal/mol; for the cubic form, $n = 2$ and $E = 25.3$ kcal/mol; for the powder, as would be expected, $n = 4$ over a wide interval of α , up to 0.70, $E = 24.6$ (orthorhombic form) and 24.8 kcal/mol (cubic form); the values of E for tablets are practically identical for both forms, but considerably greater (30.1 and 29.9 kcal/mol), and $n = 3$ (for the orthorhombic form) in the interval of α from 0.05 to 0.75.

For small α , this dependence can be approximately expressed by a power formula with an exponent of $n = 4$, which was produced by Galvey and Jacobs in contrast with Bircumshaw, whose experiments indicated a figure of 6.

From the integral activation energies produced, we can calculate E_1 for the formation of seeds and E_2 for their growth. For crystals, $E_1 = 31.7$ and $E_2 = 16.3$ kcal/mol, for powder and tablets E is equal to 22 and 30.1 kcal/mol respectively. These great differences are attributed by these authors to differences in the physical structure of the bonding elements in the material mosaic.

Above 240°C, i.e. in the cubic form, ammonium perchlorate decomposes identically in crystals, powder and tablets ($n = 2$ in the value of E amounts to 25.3, 24.6 and 29.9 kcal/mol respectively). This is related to the fact that the modification transition removes the differences which were determined by the preparation of the specimen.

In one work [102], the decomposition of ammonium perchlorate was performed in a closed vessel, but without freezing of the condensed products, with measurement of the pressure by a Bourdon type manometer. The course of decomposition was determined by curves of $p(t)$, recalculating pressure per unit volume under normal conditions. In the interval 160-280°C, the general course of the curves was S-shaped (Figure 70, 71) and includes induction period OA, a period of rapid increase in rate AB, a slow decrease BC, a sector of constant or very slow decrease in rate CD and a period of ordinary, that is relatively rapid decrease DE.

The first three periods encompass a small portion of the decomposition and can be clearly observed only at relatively low temperatures (160-200°C). Thus, the induction period, with which amounts about 1,000 min at 160°, decreases to 100 min at 190°; the period of acceleration is completed after 2600 min at 160°, where $\alpha = 0.026$, and after 50 min at 230°C with a degree of decomposition ~ 0.09 .

Thus, the lower the temperature the shorter (in degree of decomposition) the acceleration stage. The principle portion of the decomposition process, particularly at high temperatures, is made up of the constant rate period, which is completed at $\alpha = 0.91-0.98$. A change in the degree of filling of the vessel with perchlorate (m/v) has no essential influence on the course of decomposition, nor does the presence of an inert gas (400 mm N_2). The course and rate of decomposition change only slightly with a change (by 70 times) of the dimensions of the perchlorate particles.



Figure 70. Decomposition of ammonium perchlorate at $m/v = 10 \cdot 10^{-4}$ g/cm³ (190°C). 1 and 2, pure products; 3, beneath layer of paraffin.

During the acceleration sector, the rate increases in proportion to the pressure to a degree which increases with increasing temperature and lies between 3.2 (at 180°) and 3.8 (at 210°). The decrease in rate can be described by an expression for the compressing sphere. The later constancy of the rate is apparently a result of two influences--the decrease in rate due to decreasing quantities of reaction materials and its increase due to the "rejuvenation" effect of the decomposition end products. This effect

appears slightly during the initial stages of decomposition, when the content of condensing components²⁵ is small and the quantity of perchlorate requiring "rejuvenation" is small. The "rejuvenation" can be confirmed by freezing the decomposition products which condense as was observed in the experiments of Bircumshaw, as well as by the presence in the vessel of paraffin or hexane vapors in sufficient concentration. The initial stages of decomposition in the presence of these materials do accelerate, but afterward the process stops or, more precisely, is very strongly retarded--the rate of gas formation is decreased by a factor of 20 (Figure 70 and 72). Interruptions of the experiment involving temporary cooling of the reaction vessel lead, as a result of "rejuvenation" to a temporary acceleration of decomposition; in the presence of paraffin, this acceleration is not observed.

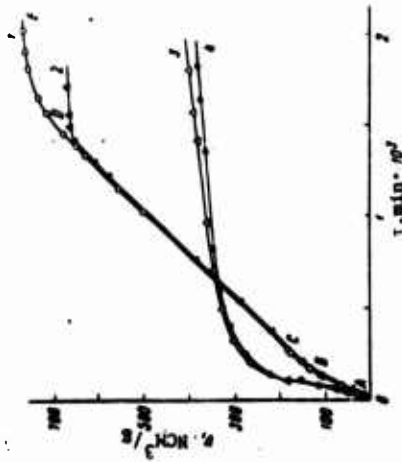


Figure 71. Decomposition of ammonium perchlorate at $m/v = 10 \cdot 10^{-4} \text{ g/cm}^3$ (250°C). 1 and 2, pure products; 3 and 4, beneath paraffin layer.

Other, more chemically active organic impurities accelerate the decomposition through the first third, but then, like paraffin, retarded. Some of them, however, do not have this influence in the temperature area of stability of the orthorhombic modification, but show this effect strongly at 240°C and higher. Then, increasing the temperature to the area of the modification transition is accompanied by a sharper decrease in rate than is produced by the perchlorate without the impurities (Figure 73 and 74).

²⁵ See p. 133

The temperature dependence determined during various decomposition sectors is expressed by an Arrhenius straight line; the value of E using various formulas and for various sectors is similar and lies between 26 and 31 kcal/mol; for decomposition beneath a layer of paraffin, the curves of $p(t)$, in contrast to the perchlorate itself, match well over their entire length (Figure 73 and 74) according to the matching coefficient $E = 25.1 \text{ kcal/mol}$.

The absolute value of rate is also not great; at 270°C the half decay period is 225 min, which is much greater than, for example, for the decomposition of ammonium nitrate. A definite role here can be assigned to the different states of the materials.

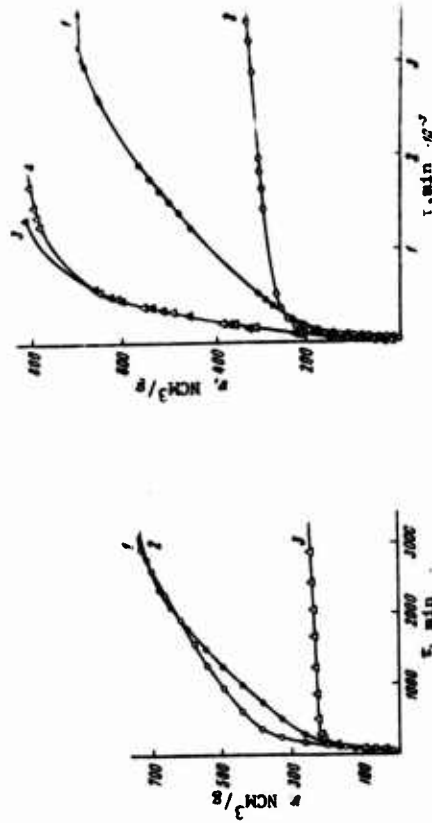


Figure 72. Decomposition of ammonium perchlorate in the presence of normal hexane at 220°C with $m/v = 10 \cdot 10^{-4} \text{ g/cm}^3$. 1, without hexane; 2, hexane pressure 40 mm Hg; 3, hexane pressure 450 mm Hg.

Figure 73. Decomposition of ammonium perchlorate (1), its mixture with paraffin (2) and with material B (3 & 4) at 220°C with $m/v = 10 \cdot 10^{-4} \text{ g/cm}^3$.

The decomposition of ammonium perchlorate was also studied [100] at high temperatures (380-450°C). The curves showing changes in pressure with time at these temperatures differ considerably from those observed at lower temperatures; there is no acceleration sector, and the rate decreases over the entire duration of decomposition, which does not stop at 30%, but rather continues to

completion. These curves can be expressed by the formula $p = kt^n$, where n is less than 1 but increases with increasing temperature from 0.5 at 380-400° to 0.8 at 450°C.

Subsequently, high temperature decomposition was studied in greater detail and using a slightly different method [104]. The experiments were performed in a glass vessel in which, after evacuation, a certain quantity of nitrogen was introduced, in order to delay sublimation; the course of the process was recorded using a quartz spiral weighing device.

At 300-380°C, the experiments gave no reproducible results. Above 340°, the reaction was retarded throughout its entire length and showed no characteristics of stoppage until completion. At 400-440°C, reproducible results were produced, with practically no residue. The rate constant was proportional to the nitrogen pressure to a power of 0.6. The curves are expressed by the equation $\frac{2}{3} = kt + \text{const}$, where m is the mass of the undecomposed salt. According to the temperature dependence of the rate constant, calculation gives an activation energy of 73.4 kcal/mol.

In the area of relatively high temperatures, decomposition of the perchlorate was studied in the presence of an inert gas (nitrogen) by Galwey and Jacobs as well [103]. The pressure of decomposition products was measured by a spiral glass manometer. They confirmed that decomposition occurs according to a power law $p = kt^n$, where $n < 1$. With increasing charge, n decreases slightly (chunks of pressed tablets were used); sometimes, the curve of $p(t)$ consists of two sectors with different n , less at the beginning. Analysis of experimental data using the compressed envelope formula $1 - (1 - a)^{1/3} = kt$ showed constancy of k over a considerable interval of a for tablet chunks from 0.2 to 0.8 and for whole crystals from 0 to 0.7. The activation energy for the tablets calculated using this formula was 38.8 kcal/mol.

Analysing the results produced, Bircumshaw sees three competing reactions, occurring during heating of the perchlorate: a low temperature reaction, a high temperature reaction and sublimation. The first of these must be considered a reaction occurring in the solid phase with typical points of such a reaction. The high temperature reaction (380-440°C) must be considered the decomposition of the perchlorate vapors, which is indicated by the influence of the inert gas pressure on this reaction. The leading reaction is probably the decomposition of the ClO_4^- -ion. This is indicated by experiments with potassium perchlorate, which yield an activation energy at 500-550°C = 69.3 kcal/mol and near

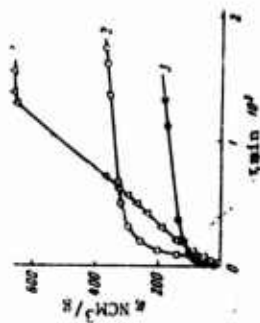


Figure 74. Decomposition of ammonium perchlorate (1), its mixtures with paraffin (2) and with material B (3) at 250°C and $m/v = 10 \cdot 10^{-6} \text{ g/cm}^3$.

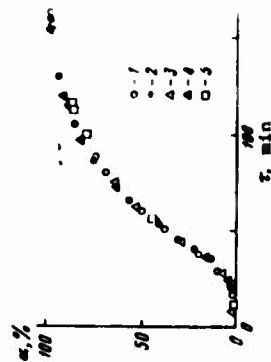


Figure 75. Matching of curves of $v = f(t)$ by time axis for paraffin mixture during stage of rapid increase in pressure. Transformation coefficient at various temperatures: 1, 180°C, 18.5; 2, 190°C, 8.6; 3, 200°C, 5.4; 4, 220°C, 1.7; 5, 230°C, 1.

the activation energy of ammonium perchlorate. Also, it is difficult to imagine a different reaction for potassium perchlorate than the decomposition of the ClO_4^- -ion.

Galwey and Jacobs, in defining the stage of high temperature decomposition, considered the transition of a proton to the surface of the solid phase with subsequent oxidation of the ammonium by radicals formed in the decomposition of the perchlorate acid.

Bircumshaw justifies his conclusion concerning the three possible mechanisms for conversion of ammonium perchlorate using the following general considerations.

1. Proton transition--a reversible process which controls sublimation. If the acid is unstable, decomposition can occur by this means, as can be seen by comparing cases where the anion is NO_2 , ClO_2 , ClO_3 , MnO_4 , N_3 , with those where the anion is NO_3 , SO_4 , ClO_4 . In the first group both the acid and the ammonia salt are unstable.
2. The reaction of transition of an electron between the anion and the interstitial positive ion is an essential stage in the decomposition of alkali-earth and alkaline azides, as well as lead azide.
3. The thermal decomposition of the anion apparently occurs in the case of

the ClO_4^- ion in the perchlorate of lithium and potassium, where the chlorides are formed.

It can be considered that the NH_4^+ ion will be stable, since its possible decomposition reaction is strongly endothermic



During sublimation of ammonium perchlorate, the principle process should be proton transition. However, it is not probable that it is the initial stage of the decomposition.

The perchlorate ion can decompose thermally. Lithium and potassium perchlorates decompose at 400°C and higher, while ammonium perchlorate decomposes with measurable rate as low as 200°C . Therefore, proton transition, leading to sublimation, can explain only the high temperature decomposition of perchlorate at over 380°C . For decomposition between 200 and 300°C , the mechanism of electron transition remains.

The interstitial ions in ammonium perchlorate are NH_4^- ions, since there are much fewer of them than of the ClO_4^- ions. The initial reaction in electron transition is expressed correspondingly by the equation



The ClO_4 radical formed within the crystal either captures an electron from a neighboring ClO_4^- ion, thus diffusing to the surface where it may be decomposed, or captures a hydrogen atom, forming HClO_4 . In the first case, the point where the ClO_4 appears on the surface loses an electron and becomes a positive hole. This charge can be neutralized either by the arrival of an electron from outside the crystal, or by migration of an NH_4^- ion from a neighboring position. This NH_4^- ion becomes an interstitial ion, which can take part in the reaction of electron transfer since it is next to a decomposition point. A continuation of this process leads to the formation of a seed. The lattice within the seed must be broken, and this disruption of the lattice increases as it grows. Two effects become important in this area.

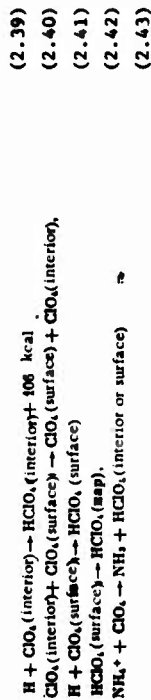
1. The electrons within the crystal reach the separation boundaries between the ordered and disordered material. This occurs due to the presence of vacancies near these ClO_4^- ions; the ClO_4 radical formed by migration of the electron may

decompose. Decomposition on the internal surface of a seed will be difficult, since during transition of an electron from ion to radical ($\text{ClO}_4^- \rightarrow \text{ClO}_4 + e$) the capture of the electron by another radical inside the crystal will be more difficult due to the disruption of the lattice and there will not be as many interstitial NH_4^- ions which can initiate the transfer on an electron due to the increasing number of vacancies at points where NH_4^- ions are located within the lattice.

2. Proton transition within the disrupted lattice will be easier, since the surface increases, that is conditions for sublimation will be favorable.

Thus, the two processes always compete for ClO_4^- ions on the surface--sublimation (by proton transfer) and decomposition (by electron transfer). The decomposition reaction forms a disrupted lattice, and this favors sublimation due to the decomposition. It is therefore possible that a certain stage of decomposition, sublimation will become much more probable than decomposition, so that decomposition stops. This explains the halt in decomposition observed.

As concerns the fate of the H-atom formed when an NH_4 radical decomposes ($\text{NH}_4 + \text{NH}_3 + \text{H} + 26 \pm 10 \text{ kcal}$) it, like the NH_3 can diffuse to the surface and go over into the volume. Another possibility is that the H-atom will meet a ClO_4 radical in the center or on the surface; in this case, HClO_4 is formed and decomposition does not occur.



Since HClO_4 within the lattice will not diffuse from the crystal as rapidly as NH_3 , it should be considered that the perchlorate decomposed will be slightly acid, which was observed. We know that traces of HClO_4 decrease the induction period, while NH_3 increases it and leads to retardation of decomposition.

It is not probable that the NH_4 in the lattice was formed by H- and ClO_4^- ions by the strongly endothermic reaction



which is therefore unrealistic at 200-300°C.

Another possible mechanism with the participation of H atoms consists of the following:



Thus, the H atoms can react either with the ClO_4 radical forming HClO_4 or with HClO_4 forming ClO_3 radicals. These ClO_3 radicals will also act like electron traps and correspondingly accelerate decomposition. This can explain the catalytic effect of HClO_4 .

The addition of ammonia may have a dual effect.

a) If there is already HClO_4 present in the lattice, NH_4 and ClO_4 ions may be formed. Since there is equilibrium between the NH_4 ions in the nodes of the lattice and the interstitial spaces, the number of the latter cannot increase too rapidly.

b) The reaction



may be reversible within the crystal. The addition of ammonia will therefore decrease the rate of formation of ClO_4 radicals and as a result of this the rate of decomposition as well. Also, it will withdraw HClO_4 molecules and possibly H atoms. The result of this will be an increase in the induction period and a decrease in the rate of decomposition in the presence of ammonia.

Galvey and Jacobs propose another mechanism for the decomposition. As the first stage, considering the composition of the decomposition products, they assume the formation and decomposition of the NH_4ClO_4 molecule, in which the stage determining the rate of the reaction is the formation of the positive hole. The decomposition of the molecule involves the splitting of water, formation of a nitrogen atom and ClO_2 ; subsequent interaction between the nitrogen molecule and an oxygen atom (formed in the decomposition of ClO_2) produces nitrous oxide.

Influence of additives on the decomposition of ammonium perchlorate.

The influence of the oxides of a number of metals (Al_2O_3 , CaO , Fe_2O_3 , MnO_2) on the decomposition of perchlorate was studied at 230°C [94]. Manganese

peroxide has the greatest catalytic effect: 100% decomposition occurs in two hours; the decomposition curve is similar to the curve observed at 400°C except that a large quantity of ClO_2 is formed rather than nitrosylchloride. Ferric oxide also has a catalytic effect--in two hours 44% of the material was decomposed, in four hours--60% of the material. The decomposition curve is unique, having two maxima. Calcium oxide delays the decomposition, apparently as a result of the formation of ammonia. Aluminum oxide delays the decomposition, apparently as the result of the formation of ammonia. Aluminum oxide has no influence.

Galvey and Jacobs [96] studied the decomposition of mixtures of ammonium perchlorate and MnO_2 (at 137-212°C). The decomposition occurs in two stages, the first of which consists of the catalytic decomposition of ammonium perchlorate. Two constants for the two different decomposition intervals give the same $E = 32,000$ kcal/mol. This determines the mechanisms of the reaction, in which the initial stages of the formation of positive holes, while the catalytic effect of the oxide leads to an increase in the mean lifetime of the hole. The second stage in the reaction is assumed to be the decomposition of pure ammonium perchlorate, which is independent of the presence of the catalyst.

The effect of the catalyst (MnO_2 , Ni_2O_3 , MgO and a mixture of the oxides of cobalt $\text{Co}_2\text{O}_3 + \text{Co}_3\text{O}_4$) on the thermal decomposition of ammonium perchlorate was also studied in connection with their influence on combustion by Hermoni and Salmon [97]. At 170-200°C, decomposition was studied gravimetrically, while over 200°C the pressures of nonfreezing gases ($\text{O}_2 + \text{N}_2$) are presented. All of these oxides accelerate the decomposition of ammonium perchlorate at 170°C, and cobalt oxides are particularly strong in this respect. The effect of magnesium oxide is decreased as its content is increased, obviously as a result of its interaction with the ammonium perchlorate, forming magnesium perchlorate.

Above 200°C, an increase in the quantity of MnO_2 (above 5%) has almost no effect on the rate of decomposition, but the final pressure did increase slightly. The rate of gas formation during the stage of decrease can be described by the compression envelope equation. The calculated value of E changes for different catalysts between 27-48 kcal/mol and is higher at increased temperatures (Table 10) which may be connected with a change in the

decomposition mechanism. The presence of catalysts influences the reaction both in the condensed and in the gas phases; catalysts also change the composition of the gaseous decomposition products, which depends also on the temperature.

Table 10
Arrhenius Parameters A and E Produces in Various Temperature Intervals.
(100 mg ammonium chlorate + 15 mg catalyst)

Catalyst	Temperature Interval, °C	B	E, kcal
NaO ₂	170-200	4.40 ¹²	38
Na ₂ O ₂	170-200	3.40 ¹²	33
CaO ₂ + CaO ₂	170-200	9.40 ¹²	33
Na ₂ O ₂	210-235	3.40 ¹²	43
NaO ₂	200-240	10 ¹²	24
CaO ₂ + CaO ₂	210-230	1.540 ¹²	42
CaO ₂	210-230	1.40 ¹²	27
Na ₂ O ₂	249-272	10 ¹²	48
Na ₂ O ₂	245-265	8.40 ¹²	40
CrO ₃	250-275	1.40 ¹²	38

Decomposition was complete throughout the temperature interval studied. The catalyst shortened the time to flash more strongly the more catalyst was present (to a certain limit); with large grain perchlorate, the amount of catalyst required for maximum shortening of the delay time was less; the delay time to flash was also decreased by increasing the exterior pressure.

Galvey and Jacobs [98] also studied the influence of charcoal on the decomposition of ammonium chlorate. At below 240°C, the charcoal did not influence the decomposition and did not react with its products. At 240-260°C, it reduced the induction period, above 260°, decomposition is accelerated rapidly and leads to a mild, flameless explosion, accompanied by breakage of the tablets. The pressure during the decomposition increases exponentially with an exponent of > 1, depending on the mass of the tablet and increasing with temperature, apparently as a result of self-heating. The authors noted that in the presence of charcoal, the decomposition does not stop at 30% beginning at 240°, as opposed to 350° for pure perchlorate²⁶.

The influence of cuprous oxide on the thermal decomposition of ammonium chlorate has been studied [99]. Fragments of pressed tablets were decomposed

²⁶ See p. 133.

at 265°C at a nitrogen pressure of 250 mm, beginning with a short induction period, the rate constant and degree of decomposition are independent of pressure. The course of the decomposition is described by the expression

$$\lg(1-\alpha) = (kt)^n \quad (2.33)$$

A mixture with Cu₂O (4.56 molar %) at 260°C showed an exponential pressure increase at first, followed by an even more rapid increase, ending with a flash after 540 sec. With smaller charges and lower temperatures, the curve of p(t) is S-shaped, and a slight pressure drop is observed after the maximum. E, calculated by the rate of gas formation at various temperatures, was 29.0 kcal/mol, or, when calculated by the delay time to flash, 28.1 kcal/mol. The time to flash depends in a complex manner on the content of Cu₂O, apparently as a result of the multi-staged nature of the process in the presence of Cu₂O, which can be determined from the curves of p(t) up to flash formation at various levels of cuprous oxide contents.

VIII- General Regularities in the Thermal Decomposition of Explosives

The investigations which we have analyzed allow us to make certain general conclusions concerning the mechanism and specific features of slow thermal decomposition of explosives.

It has been established that the thermal decomposition of many explosives generally consist of a combination of at least two reactions. One of these is spontaneous, and is a first order reaction for the material studied in this respect, its rate depending only on the temperature of the material and corresponding to the minimum possible decomposition rate.

The second reaction is a self-accelerating reaction using the autocatalytic or some other mechanism, in which case the material causing the acceleration may either be the end product of decomposition (for example, water in the case of the nitroesters) or an intermediate product (for example, nitrogen dioxide in the decomposition of nitroesters).

If the products which accelerate the reaction are nonvolatile materials, both reactions--the primary and self-accelerating reactions--occur at the same time. If these products are volatile at the decomposition temperature, then under certain conditions (high temperature, high relative volume of vessel, passage of a current of inert gas, etc.) they may be removed from the condensed phase, and the monomolecular reaction may be observed in its pure form.

Suppression of the self-accelerating reaction can in principle be achieved with nonvolatile catalyst as well, by adding impurities (stabilizers) to the explosive which react with the autocatalysts and minimize the accelerating effect. Finally, in order to study the primary reaction, the initial stages of decomposition may be used, during which the concentration and effects of decomposition products are slight.

Studying the temperature dependence of the rate of the monomolecular reaction, we can establish the kinetic constants of this reaction: the activation energy E , the factor before the exponent B and the half-decay period, giving us a clear representation of the maximum possible comparative stability of any given explosive material. The first such analysis of the kinetics of the monomolecular decomposition of explosives was performed by Roginskiy using his own experimental data and the materials of preceding work. This analysis discovered certain unique kinetic specific features of the decomposition of explosives.

Explosives decompose with a noticeable, measurable rate at moderately high temperatures, 100-300°C, i.e. their rate constants of decomposition are rather high. At the same time, this decomposition is characterized by a high temperature rate factor: the rate of decomposition increases by approximately 4 times for many explosives with a temperature increase of 10°C. This great temperature dependence of the rate naturally indicates high activation energy.

Actually,

$$\begin{aligned} k_0 &= B \cdot e^{-E/RT}, \\ k_1 &= B \cdot e^{-E/RT}, \end{aligned} \quad \begin{aligned} (2.46) \\ (2.47) \end{aligned}$$

The temperature rate factor

$$\frac{k_0}{k_1} = \frac{e^{-E/RT_0}}{e^{-E/RT_1}} \quad (2.48)$$

Logarithmizing, we produce

$$\begin{aligned} \ln \frac{k_0}{k_1} &= -E/RT_0 + E/RT_1, \\ \ln \frac{k_0}{k_1} &= \frac{E}{R} \cdot \frac{T_1 - T_0}{T_0 T_1}, \end{aligned} \quad \begin{aligned} (2.49) \\ (2.50) \end{aligned}$$

from which

$$E = R \ln \frac{k_0}{k_1} \cdot \frac{T_0 T_1}{T_1 - T_0} \quad (2.51)$$

Thus, if with a given value of the product $T_1 T_2$ the ratio k_2/k_1 is great, E should also be great. On the other hand, since the value of k is considerable, with great E , the value of $B = k e^{E/RT}$ should also be great. Actually, as we can see from Table 12, for many explosives the value of E is great, between 40,000 and 60,000 cal/mol; the same is true of the value of B which for many explosives lies between 10^{16} and 10^{28} .

The fact that the activation energy of explosives is great is not in itself surprising. The capability of exploding naturally means instability of the molecules, but is determined by the relationship between the energy of the reaction causing excitation of the reactions of neighboring molecules and the activation energy, which measure the stability of the molecule in relation to energetic effects.

The same cannot be said concerning the high values of the constant B . According to the generally accepted concepts, B cannot be much greater than the frequency of intramolecular oscillation $10^{12}-10^{14}$. Therefore, the establishment by Roginskiy for all explosives studied at the time of much greater values of B was of considerable interest. It could be assumed that this regularity is a distinguishing feature of explosives.

The natural assumption of the presence of long chains with $v = 10^6-10^7$ will explain the high values of B . In connection with this, experiments were performed with nitroglycerin consisting of decomposition in solutions, which did not confirm this assumption.

Further investigations [33, 106] showed that the high values of B are not an unavoidable feature of all explosives. Many explosives, including some alcohol nitrates, have been shown to have moderate values of E and normal values of B . Furthermore, one of the nitroesters (PETN) and one nitramine (hexogen), which produce high values of B when decomposed in the pure form, show normal values of B when decomposed in the form of solutions. All of this indicates probably that the large B are not characteristics of the monomolecular reaction, but result from certain peculiarities in the course of the decomposition reaction of the individual explosives.

In [109], an increase in the quantity of gaseous decomposition products with an increase in decomposition temperature was noted, and listed as one such peculiarity. If we characterize the ratio of rates at two temperatures by the

ratio of absolute gas quantities liberated per unit time per unit weight of explosive, without considering the change in quantity of gases indicated, we will produce an artificially high value of temperature rate factor, and therefore also high values of E and B. The change in the nature of the curve $p = f(t)$ as temperature changes may also be a source of errors in comparison of volumes.

Another specific feature [110] of the decomposition is that it consists of two stages: an endothermic and reversible transition of the initial material A to an intermediate product B, plus an irreversible decomposition reaction of the latter $A \rightarrow B + C$. Then, as the temperature increases, the overall reaction rate increases for two reasons: as a result of the increased concentration of the intermediate product B and as a result of the increase in the rate of transition of this material to the end product C. As a result, we produce an increased value of the temperature factor and consequently higher values of E and B²⁷. Finally, other mechanisms are possible, leading to higher temperature factors. Thus, if the decomposition forms short and therefore undetectable chains, the length of which increases with temperature, if self heating occurs increasing with an increase in temperature, if the concentration of the volatile autocatalyst in the liquid phase increases with increasing temperature due to the fact that the rate of diffusion increases with increasing temperature more slowly than the rate of the reaction, all of these factors may lead to increased values of E and B.

A clarification of these problems should be the subject of further experimental investigations. In any case, many typical explosives do not show any essential differences from nonexplosive materials as concerns the characteristics of their monomolecular reaction.

The self accelerating decomposition of explosives is incomparably more complex. Usually, this self acceleration decomposition is analyzed as autocatalytic. However, only in a few cases (trityl, tetryl, hexogen) has the formation of autocatalysts been confirmed by direct experiments by addition of the reaction products to the fresh material, leading to an increase in the rate of gas formation. Even in this case, only for tetryl has the course of the decomposition been found to agree with a simple autocatalytic reaction plan, the rate of which

²⁷See p. 133.

is proportional to the first power of the concentration of the autocatalyst.

It is possible that in many cases the acceleration of gas formation during decomposition is a result of the fact that it represents a combination of successive reactions, including the formation of unstable intermediate products, which decompose at a higher rate than the initial material. The rate of formation of gases (or heat) in the decomposition will increase with time also if the conversion of the intermediate product produces gases (or heat) in considerably greater quantities than the primary conversion of the initial material.

It is particularly probable that the decomposition occurs as a series of successive reactions in the case of decomposition of explosives containing several identical groups, with which the decomposition of the molecule begins--the polynitrates of polyhydric alcohols, polynitro-compounds, etc. Naturally, the first process in this case is the reaction of one group, which does not necessarily lead to immediate decomposition of the molecule. Of course, this does not exclude the possibility of autocatalytic influence of the decomposition products, both the end products and intermediate products. This influence is complicated by the fact that certain catalyst are volatile and their concentration in the liquid phase depends on the experimental conditions, which determines the pressure of the gases over the liquid.

If we consider that the varied direction of the reaction, inasmuch as we can determine it from the final composition of the reaction products, changes with a change in temperature, the complexity of the decomposition under self acceleration conditions becomes clear. We add that the composition of the decomposition products in all cases studied does not correspond to the equilibrium concentration, so that a change cannot be explained by the influence of temperature on equilibrium.

The thermal decomposition of explosives in the solid state, while it is similar in principle to the decomposition of liquid explosives, as two peculiar features. First of all, the reaction begins with the appearance of seeds, primarily on the surface of the explosive crystals. These seeds grow unevenly in the material. Secondly, the reaction frequently has not one, but two rate maxima. Apparently, both of these facts influence essentially the mechanism of combustion of such explosives. For those solid explosives which can be melted, it has been established that the rate of decomposition in the liquid state is

considerably higher than in the solid state. If condensed products are formed during decomposition and the solid explosive material, dissolving in them, partially goes over to the liquid state, this leads to progressive acceleration of the reaction regardless of other possibilities for its acceleration.

We note in conclusion that almost all investigations of the thermal decomposition of explosives have been performed manometrically. This method has been used not because it is most suitable for the study of the course of decomposition, but rather only because of its simplicity and easy availability. At the same time, this method gives us only the summary result of complex reactions and that only to the extent that each of the reactions is accompanied by the liberation of gases which do not condense at the experimental temperature. Using the total gas liberation to judge the course of individual reactions is possible only in exceptional cases. Therefore, in the methodological respect, the experimental investigation of the thermal decomposition of explosives needs considerable improvement.

The mechanisms of chemical conversion of explosives which we have analyzed--monomolecular and self-accelerating--have been studied for the slow, homogeneous thermal decomposition of explosives. The question naturally arises, to what extent they occur during the burning of explosives. Doubtless, during the initiation of burning--when explosives are ignited or reach their flash point--self-acceleration processes have an important role to play. It is due to the gradual development of self-acceleration of a reaction that thermal equilibrium is disrupted--the heat input becomes greater than heat output, after which decomposition is accelerated rapidly by a thermal mechanism until combustion occurs. However, during autocatalytic self-acceleration, the role of the autocatalyst in the formation of a flash or burning is also determined by the temperature of the explosive and rate at which this temperature is reached.

With rapid heating, the reaction rate critical for the thermal mechanism can be achieved due to the monomolecular reaction in such an early stage that the concentration and effect of catalyst is not noticeable. Also, as the temperature increases the value of the constant of monomolecular decomposition increases more rapidly than the value of the constant of autocatalytic reaction, in correspondence with the differences in the activation energies, and at high temperatures, therefore, the relationship of the rates is less favorable for autocatalysis than at low temperatures.

Under ordinary conditions of stable combustion, this condition is apparently fulfilled, and during the combustion of many explosives, particularly volatile explosives and at low temperatures, autocatalysis in the liquid phase has no essential role to play.

The problem is less clear for nonvolatile explosives, including nitrocellulose. In this case the surface and autocatalytic reactions might apparently have a greater role to play, determining the essential difference in the combustion mechanism of nonvolatile explosives from the mechanism of combustion of volatile explosives.

Table 12

Activation Energies, Exponential Factors and Half Decomposition Period for Various Explosives

Explosive	Temperature Interval, °C	E, cal/mol	log, B	Half decomposition period at 120°C, calc., hours	Reference
Methylnitrate	212-239	39,500	14.4	7120	[105]
Nitroglycerol	161-181	41,230	16.25	922	[106]
		35,000	14	56	[107]
Nitroglycerin	85-105	39,000	15.9	119	[108]
	150-190	50,000	23.5	3.91	[11]
	125-150	45,000	19.2	129	[11]
	90-125	42,500	18.0	95	[11]
	75-105	40,300	17.1	40	[108]
	90-120	43,700	18.64	80	[9]
Nitroglycerin at low δ	80-140	43,700	18.4	140	[16]
Nitroglycerin at high δ	80-140	39,300	15.4	540	[16]
Propylene glycol dinitrate	80-100	37,400	15.2	77	[108]
Trimethylene glycol dinitrate	85-110	38,100	15.2	188	[108]
Triethylene nitromethane nitrate	75-95	36,400	15.3	17	[108]
PEM at low δ	160-225	47,000	19.8	421	[33]
PEM in solution	145-171	39,000	15.6	230	[32]
Diethylene glycol dinitrate	171-238	39,500	15.1	142	[33]
Dina	60-150	42,500	16.5	2400	[35]
Ethylenediamine dinitrate	100-160	42,000	16.5	1400	[36]
Ammonium nitrate	230-357	40,000	13.1	27.10 ⁴	[33]
Pyroxyline No. 1 (13% N)	243-361	40,500	13.8	10 ⁵	[33]
Pyroxyline No. 1 (13% N)	90-135	49,000	21.0	343	[11]
Pyroxyline No. 1 (13% N)	140-155	48,000	20.0	954	[11]
Pyroxyline No. 1 (13.35% N)	155-175	56,000	24.0	2680	[11]
Same	135-160	39,200	15.0	1200	[44]
Pyroxyline No. 2 (12.3% N)	70-160	39,500	15.35	770	[43]
Collodion (11.85% N), solution	70-160	38,500	14.4	1900	[43]
Collodion cotton	165-200	43,000	18.0	150	[40]
Ethylene dinitramine		50,000	21.0	1230	[11]
Mononitrobenzene (vapor)	184-254	30,500	12.8	2.8**	[64]
Dinitrobenzene (vapor)	390-415	53,400	12.65	17.10 ¹²	[60]
Trinitrobenzene (vapor)	346-355	52,600	12.70	6.10 ¹²	[60]
Trinitrobenzene (liquid)	270-355	51,900	13.60	3.4.10 ¹¹	[60]
Trotyl (vapor)	250-310	43,000	10.9	1.9.10 ⁹	[60]
Trotyl (liquid)	280-320	34,500	8.45	107	[60]
Trotyl	193-250	26,200	-	-	[60]
Trotyl	220-270	53,500	19.0	5.8.10 ⁶	[11]

(Continued)

Table 12 (Continued)

Explosive	Temperature Interval, °C	E, cal/mol	log, B	Half decomposition period at 120°C, calc., hours	Reference
Trinitroaniline (vapor)	250-320	38,500	8.8	7.5.10 ⁴	[60]
Trinitroaniline (liquid)	250-300	31,000	7.1	2.6.10 ⁴	[60]
Picric acid	-	57,500	23.0	18.10 ⁴	[11]
Hexanitrodiphenyl sulfide	240-300	49,500	16.1	4.9.10 ⁷	[60]
Liquid	235-255	43,000	15.5	4.9.10 ⁴	[60]
Solid	200-220	42,700	12.0	9.7.10 ⁷	[60]
Medina	110-130	35,400	15.6	2.3	[65]
Hexogen in solution	213-299	47,500	18.5	16.10 ³	[70]
Hexogen	-	41,000	15.46	4.2.10 ³	[70]
Hexogen in solution	150-197	51,000	18.6	1.1.10 ⁶	[71]
Hexogen in solution	150-197	41,300	15.3	8.2.10 ³	[71]
Octogen	-	52,700	19.7	7.8.10 ⁵	[70]
Octogen in solution	176-230	36,500	10.7	7.2.10 ⁵	[71]
Liquid tetryl	176-230	42,600	14.9	1.1.10 ⁵	[71]
Same	129.9-138.6	60,000	27.5	142	[11]
Same	211-260	55,500	24.5	447	[11]
Same	-	38,400	15.4	174	[64]
Same	-	52,000	22.5	505	[11]
Trinitrotriazidobenzene	20-100	32,300	12.7	8700	[84]
α -lead azide	245-275	55,000	-	-	[74]
Same	220-260	38,000	-	-	[82]
8-lead azide	237-252	40,000	-	-	[79]
Same	200-270	37,000	-	-	[82]
Lead trinitroresorcinate	225-255	46,700	-	-	[84]
Fulminate of mercury	100-115	25,300	-	-	[77]
Sodium azide	240-275	34,400	-	-	[82]
Potassium azide	222-255	36,100	-	-	[82]
Calcium azide	60-130	18,000-19,000	-	-	[82]
Same	80-100	20,000	-	-	[82]
Strontium azide	100-135	20,200	-	-	[82]
Barium azide	100-150	23,500	-	-	[82]
Silver azide	210-270	29,000	-	-	[82]
Same	-	40,000	-	-	[82]

* Half-decomposition period calculated from data produced for state material at temperature shown in column 2, i.e. at 120°C.

** The short half decomposition period of ethylene dinitramine is because data used [64] were from melt, which decomposes much more rapidly than solid material.

Footnotes

1. To p. 5. Frequently, the degree of filling of the vessel is characterized by the rate ratio of explosive to the free volume (m/v). Since $m/v = d \cdot \delta / (1 - \delta)$, where d is the specific gravity of the explosive material, at low values of filling of the vessel δ is proportional to m/v .
2. To p. 10. Another explanation for the dependence of critical pressure on δ is given in [18].
3. To p. 11. Gorbunov determined also the solubility of water at 120°C in diglycol dinitrate and dinitroglycerin; in the former it is less than in nitroglycerin (solubility constant $6.6 \cdot 10^{-6} \text{ mm}^{-1}$ for nitroglycerin and $5.2 \cdot 10^{-6} \text{ mm}^{-1}$ (for diglycol dinitrate), while in the latter it is considerably greater; $36 \cdot 10^{-6} \text{ mm}^{-1}$.
4. To p. 17. If the nitroglycerin is decomposed in the presence of oxygen, acceleration begins more rapidly, apparently due to the conversion of the nitrogen oxide formed in reduction back into the dioxide.
5. To p. 21. The ratio of rates in the liquid and solid states increases as the temperature decreased; at 130° it is 40, at 110° it is 100.
6. To p. 28. However, comment should be noted that the activation energy of the decomposition of N-nitromins is approximately the same.
7. To p. 40. According to the investigations of Ville [10], curves of decomposition of incompletely stabilized nitrocellulose are similar.
8. To p. 44. A certain retardation of the first stage is observed later, more strongly the higher the initial pressure (Figure 33).
9. To p. 59. The temperature intervals were taken such that the rate of gas formation could be easily measured by the method used.
10. To p. 83. Experiments of Yu. P. Zakharov with constant charge (0.5 g) at m/v between 0.15 and 0.44 g/cm^3 (180°C) show that the time to ignition was practically independent of m/v . It is therefore possible that in this case the determining factor is the explosive charge size, not the influence of ampule volume.
11. To p. 84. Preliminary experiments have shown no essential influence of this factor on ignition.

12. To p. 86. It is possible that during the decomposition of nitromines the primary process is, as in the decomposition of nitroesters, the splitting of NO_2 .
13. To p. 87. This conclusion differs with the results of a later work by Maksimov [71], who determined a considerable increase (by 2-5 times) in the rate of gas formation in the initial sector for solutions of hexogen in dinitrobenzene at 150-200°C; the acceleration depends on the m/v ratio which, possibly, reveals the reason for the difference; also, Robertson & his experiments with solutions eliminated the initial sector from analysis, and it is during this sector that the heating and evaporation of the solvent occurs.
14. To p. 88. During decomposition partial, and at high temperatures (197°C) total liquification of the material can be visually detected, which causes the charge to be caked; this melting probably is one of the reasons for the acceleration of gas formation noted.
15. To p. 94. The formation of black seeds, which can be easily seen against the white crystalline aggregates, can be observed visually even with slight magnification.
16. To p. 95. It should be added that according to other works [73] the decomposition of silver oxalate follows the chain rule during the acceleration stage. It cannot be excluded that the cause of the difference is differences in the preparation conditions of the salt.
17. To p. 97. It should be noted that data on the type of decomposition of lead azide are contradictory. In addition to the observations of Garner [82] which indicate rapid onset of the stage of decrease in the rate, there are also data by the same author which indicate a considerable sector of great increase if crystals of smaller dimensions and lower temperatures are used. Apin [79] definitely observed long induction periods and an exponential increase in gas formation upon decomposition of lead azide over a broad temperature range.
18. To p. 98. It should be indicated that it is not always possible to select between exponential and logarithmic increases. Thus Garner, who first included fulminative mercury and barium azide among those materials characterized by exponential increases of rate with time now considers it proper to express this growth by a logarithmic dependence.

THEORY OF STABLE COMBUSTION OF EXPLOSIVES

1. Mechanism of Combustion

The chemical conversion of an explosive to the products corresponding to thermodynamic equilibrium is exothermic. If this exothermic conversion is without energy losses to the surrounding medium, the temperature of the system must be increased. Since the rate of the reaction increases rapidly with temperature, the chemical conversion of explosives under certain conditions is self-accelerating. Under actual conditions, when heat losses do occur to the surrounding medium, the condition of self-acceleration is heating of the explosives to a certain critical temperature, beginning at which the heat input due to the heat from the reaction exceeds heat losses. The excess of heat input over heat losses will be retained at all higher temperatures achieved by the explosive as a result of self heating. This is the essence of the theory of thermal explosion [2, 223].

The critical temperature is that minimum temperature which, when it is reached, assures that the reaction will continue spontaneously to the stage of flame development. This development, since it begins at a relatively low temperature, occurs comparatively slowly and the flame stage occurs after a noticeable delay.

The theory of the thermal explosion analyzes the case in which a certain volume of explosive material is evenly heated by an external heat source, as heat exchange occurs between this volume and the surrounding medium. The heat input and heat output are in stable equilibrium if the heat output increases more rapidly with temperature than the heat input, and conversely the equilibrium is unstable if the heat input increases more rapidly than heat output. In this latter case, the reaction rate increases to very high values, corresponding with the maximum temperature reached in the reaction.

An analogous phenomenon can occur if only a small surface layer of the explosive is heated.

Let us assume for simplicity that the explosive has the form of a cylinder, that the heat loss in the radial direction is nil and that heating is performed for the surface layer of the explosive on one end of the cylinder. In this case,

19. To p. 100. One exception is disubstituted potassium styphnate, for which the acceleration increases with increasing experimental temperature.

20. To p. 104. When ammonium picrate and styphnate decompose, an increase in the m/v ratio decreases the initial rate.

21. To p. 106. The specific surface of the residue [95] was $1.5 \text{ m}^2/\text{g}$, corresponding to a particle size of 3.

22. To p. 106. The composition of constant gases was practically identical over a broad temperature range (240-330°C) and throughout the course of an individual experiment, which allowed their quantity to be used as a measure of the extent of decomposition.

23. To p. 108. Ammonium perchlorate was stored in a vacuum during the interruption.

24. To p. 110. The fact that the Prent-Thompkins equation is still applicable in this interval under certain decomposition conditions is explained by Galwey and Jacobs by the possibility of branching of the reaction propagating along the bonding material at points of contact of several crystallites.

25. To p. 113. The content of condensed products increases during the decomposition, apparently as a result of gas phase reactions; when one half decomposition is reached, it amounts to ~50% (at 20°C) and ~80% (at ~180°C) and subsequently remains almost unchanged.

26. To p. 121. However, it is possible that these differences result from differences in the methods used more than from the influence of the charcoal.

27. To p. 125. It should be stated that recent works on thermal decomposition of alkyl nitrates and nitrites (see p. 42), showing that the first stage of the reaction is endothermic and reversible, tend to confirm this statement.

the heating causes the reaction to occur and heat to be liberated. On the other hand, heat from the layer being heated is transmitted into the depth of the material, into the neighboring "cold" layer. Obviously, there is a certain temperature under these conditions at which the heat arrival will be compensated by the heat output. Beginning at this temperature, local "thermal explosion"--a rapid chemical reaction similar to homogeneous thermal explosion--will occur in this layer.

With stable combustion we have a similar phenomenon: a layer of the explosive, being heated, reaches the critical temperature. The essential difference is that the heating results not from external heat sources at a given temperature considerably lower than the combustion temperature, which therefore completes its action when the critical temperature is reached, but as a rule, continues on after the temperature is reached. Thus, the concept of the critical temperature under these conditions loses its ordinary meaning almost completely, since even after it is reached heating of the layer continues primarily due to the reaction products of the preceding layer.

The chemical reaction with rapid external heating cannot continue to any great extent at the critical temperature and primarily occurs near the maximum temperature, equal to q/c_p (heat of reaction divided by mean heat capacity of reaction products).

A thermal wave passes through the explosive as it burns, and passage of this wave causes a chemical reaction. The heat liberated by this reaction, in turn, maintains constancy of temperature distribution in space and constant propagation rate of the thermal wave. A cold layer entering the reaction zone receives heat from the preceding layer, gives heat away to the subsequent layer and is heated due to the heat of the reaction occurring. The temperature of the layer thus increases from the initial temperature to the maximum combustion temperature.

The principal factors determining the combustion rate are the temperature reached in the reaction and the rate of the reaction at this temperature on the one hand, and the rate of heat exchange between reaction products and the unreacted material on the other hand.

The rate of heat exchange is determined by, in addition to the mechanism of heat transfer (conduction, convection, radiation) and the distance of the zone of maximum temperature from the layer entering in the reaction, also by the

contact surface of the combustion products and the unreacted material. When a cylindrical charge burns at one end, the minimal area of this surface is equal to the cross-section of the cylinder; however, this area can become considerably greater, for example, if the gaseous combustion products penetrate into the depth of a powdered explosive material, if the surface ceases to be flat and takes on macro- or microrelief, if particles of solid explosive or droplets of liquid explosive enter the gas stream and are carried away by it, etc.

In addition to this, if the gaseous combustion products move in relation to the unburned material, this movement also accelerates burning, particularly if it is accompanied by turbulization on the surface of contact, which sharply increases heating of the unburned material by the combustion products.

In all of these cases the rate of burning, if it changes, becomes greater than with a flat front, since the heat of combustion from the material which has burned is more fully used to excite chemical reactions in the neighboring explosive layers. However, obviously the rate of heat exchange cannot be too great, or the temperature to which the material entering the reaction is heated would become so low that the rate of the reaction would be decreased sharply and unavoidable heat losses to the surrounding medium could not be compensated. If a tube containing burning nitroglycol is shaken, the combustion is damped for this very reason.

One criterion of the reaction rate as it occurs evenly throughout the entire volume of an explosive might be the flash point. However, the "flash" point--the temperature of equilibrium of heat input and heat output--must be higher as applicable to combustion conditions than during homogeneous thermal explosion, for two reasons. The material in this case is subjected to heating on one side and at the same time heat is given off into the depth of the cold material, while during the excitation of a homogeneous thermal explosion the entire volume of the explosive is surrounded by a medium of increased temperature. On the other hand, during the homogeneous process heating usually occurs slowly, and the reaction rate increases not only as a result in the increase in the temperature, but also due to isothermal self-acceleration of the reaction.

The fact that the flash point is inconstant in its own definition is clear without explanation. The arbitrariness of the flash point as a criterion for reaction rate during combustion also results from the difference in the mechanism of flashing and combustion, analyzed above. However, under certain

conditions, we can obviously analyze the process of combustion as a continuous series of flashes of successive explosive layers, heated by the reaction products to a certain critical temperature, at which a sudden change in the state of the explosive occurs, as a result of which the layer ceases to transmit heat to the underlying layers or at least this transmission is strongly decreased.

For example, this is the situation if the explosive can be vaporized, which sharply reduces heat transmission in comparison with heat transmission through a liquid, or if the explosive is dispersed, converted into a suspension of particles in the gaseous conversion products. This change in the state of the explosive can be looked upon as a result of rapid development of reactions similar to flashing, as a result of chemical self-acceleration, which can be accompanied by an increase in heat liberation. Under these conditions, the combustion rate can be looked upon as the rate of heating of the material from its initial temperature to the critical temperature.

This is the way in which Michelson, Mallard and LeChatelier [224] concluded expressions for the burning rate, after analyzing this case as the general mechanism of the combustion process.

II. Hypothesis of Michelson and Mallard-LeChatelier

If combustion products at a temperature of T_g heat a layer of gas (or explosive¹) at temperature T_0 to the flash point T_k , then, equalizing the quantity of heat

$$q_1 = \alpha(T_g - T_0), \quad (4.1)$$

given off by the combustion products to the unburned gas (explosive), the quantity of heat received in one second will be

$$q_2 = u\delta\alpha(T_g - T_0), \quad (4.2)$$

$$\alpha(T_g - T_0) = u\delta\alpha(T_g - T_0), \quad (4.3)$$

and we arrive at the relationship

$$u = \frac{\alpha(T_g - T_0)}{\delta\alpha(T_g - T_0)}, \quad (4.4)$$

where α is the heat transfer coefficient; δ is the heat capacity by volume; δ is the density of the gas (or material).

¹ See p. 184.

Since

$$T_g - T_0 = \frac{Q}{c_1}, \quad (4.5)$$

where c_1 is the specific heat capacity of the combustion products, then

$$u = \frac{\alpha Q}{\delta c_1 (T_g - T_0)}. \quad (4.6)$$

As applicable to condensed explosives, this formula contains the dependence of the rate of combustion on the initial temperature, which has the form

$$u = \frac{A}{T_g - T_0}, \quad (4.7)$$

or

$$\frac{1}{u} = \frac{1}{A} (T_g - T_0). \quad (4.8)$$

It also gives us the dependence of the linear rate of combustion on the cubic density:

$$u\delta = \text{const.} \quad (4.9)$$

Michelson and Mallard and LeChatelier did not analyze the dependence of the rate of combustion on pressure. The increase in the rate of combustion with pressure, based on the positions of their hypothesis, obviously should be interpreted as a result of an increase of the quantity of heat transmitted by the products of combustion to the explosive material with increasing pressure. Apparently, the experimental dependence

$$u = A + Bp,$$

established for smokeless powders, Marour [225] to believe that heat transfer during combustion is achieved by bombarding of the surface of the explosive with molecules of the adjacent gas layer which have a certain constant temperature, independent of pressure. The quantity of heat transferred is proportional to the number of impacts of gas molecules, i.e. to its pressure. Assuming also that heat transfer is performed not only by collisions of molecules but by other means as well which do not depend directly on the pressure, for example radiation from the gases and heat conducted through the condensed phase. This explains the expression of the term A in the expression for $u(p)$, which is independent of pressure.

However, at the present time the dependence

$$u = A + Bp$$

has come to use the universal nature which was attributed to it at one time; the assumption of the pressure--independence of the temperature of the gas layer adjacent to the surface of the condensed phase also cannot be considered well founded. Therefore, this aspect of the phenomenon, the influence of pressure on the burning rate, is not explained quantitatively by the hypothesis of Michelson and LeChatelier, although the increase in heat transfer with increasing density of the gas contacting the surface of the condensed phase is qualitatively quite natural.

The dependence of $u(T)$ resulting from this hypothesis in many cases agrees with the experimental facts: the inverse value of burning rate increases linearly with the initial temperature, as has been established for smokeless powders and a number of explosives. The values of T_k are similar to the flash points but higher, as should be expected. As pressure increases, T_k increases, which can also be explained by the fact that at higher burning rates, chemical self-acceleration of the reaction cannot be as fully developed.

Furthermore, in many cases the mass rate of burning of powdered explosives is independent, in agreement with the hypothesis, of the relative density of the powder; where deviations from this regularity are observed they are generally explained by the presence of an exothermic reaction in the condensed phase, by heat losses, transmission of heat along the walls of the tube, etc.

The hypothesis of Michelson and Mallard-LeChatelier was the first quantitative hypothesis suggested to explain the phenomenon of combustion. It played a significant role in the understanding of combustion and has still not lost its significance at the present time.

However, the agreement of the conclusions of the hypothesis with experimental values is not complete, and cannot be. Thus, although as a whole a certain correspondence between the combustion rate and flash point is observed for explosives with similar properties (i.e., volatile explosives) (aromatic nitrocompounds, i.e., burn more slowly than nitroesters) and between the combustion temperature and rate (nitroesters with high heat of combustion such as nitroglycerin burn more rapidly than nitroesters with low heat of combustion such as diglycidinitrate), even within the limits of these classes of compounds too many deviations are noted from this correspondence. In particular, nitroglycerin burns four times more rapidly than nitroglycol, although their flash points and heats

of combustion are similar; PETN burns six times more slowly than solid nitroglycerin. Even larger deviations are observed for the nonvolatile, rapidly burning explosives; i.e., lead trinitroresorcinate burns many times more rapidly than fulminate of mercury, although its flash point is higher than that of fulminate of mercury, and its calculated heat of combustion (per gram/atom) is considerably less. This means that the flash point is not a reliable criterion for the rate of chemical conversion during combustion. This is not surprising: the flashing of condensed explosives, with all of its schematic simplicity, is a complex process of interaction of phenomena of conversion, occurring both in the condensed and in the gas phases, strongly dependent on the relatively low temperature and slowly developing reactions of chemical conversion of the explosive. Therefore, it is hardly suitable for a characteristic of the kinetics of the conversion occurring during combustion, and we should be more surprised that the correspondence between burning rate and flash point is in many cases observed.

In addition to this, even if the flash point was determined for the small delay times which correspond to the conditions of combustion, the conception of instantaneous reaction upon reaching a certain critical temperature which is the basis of the Mallard-LeChatelier hypothesis is incorrect in principle. The reaction rate during combustion depends on the temperature and concentration, and these dependences must be taken into consideration by the theory of combustion.

We will omit the analysis of a number of later works [226-228] on the combustion of smokeless powders, which base themselves on the improper assumption that the end products of conversion during combustion arise directly at the surface of the powder. During the burning of powders the final temperature of the gases is 1000-3000°C higher than the temperature of the condensed phase and even if direct contact of these gases with the surface of the solid powder did occur, in addition to the small number of activating impacts, the overwhelming portion of the energy of the gases would be transmitted to the powder in the form of heat in portions less than the activation energy. The corresponding heating of the surface layers of the powder would be determined to a greater extent by the reaction than by direct activation of its particles. Furthermore, with this temperature difference, heat flux from gas to powder would be unrealistically great and would exceed the rate of liberation of heat by the combustion reaction.

It must be further assumed (as follows from many observations) that at any pressure, particularly at pressures measured in thousands of atmospheres, the reaction of chemical conversion of the powder or, more precisely, of the principle components of its nitroesters-nitrocellulose and nitroglycerin--do not occur in one step during combustion, but in at least two, or even more probably in a large number of steps.

This conclusion follows from the results of an experimental study of the process of combustion, particularly at low pressures. Theoretically, stepped reactions are not unavoidable; apparently, the stepped reaction is kinetically more suitable, that is each of the steps requires less activation energy than the reaction of complete decomposition. Therefore, with slow heating, in practice the reaction which occurs is that whose activation energy is least; then, the products of primary decomposition react with each other by the same means, that is along the path involving the least expenditure of activation energy, etc. until the end required by thermodynamics is reached. For certain nitroesters, probable plans for the individual steps have even been developed.

It should be kept in mind here that the first step in the decomposition is either endothermic or weakly exothermic. Therefore, the assumption of direct contact of the products of a complete conversion reaction, with the maximum burning temperature, with the surface of the condensed phase during combustion is quite inaccurate. The zone of maximum temperature is separated from the surface of the condensed phase by a rather thick layer of gases, in which heating and chemical conversion are occurring. The transmission of energy to the condensed phase occurs in the simplest case by heat conductivity through this gas layer. Here, the temperature of the surface layer of gases adjacent to the surface of the condensed phase is only slightly (a few degrees) higher than the temperature of the surface, so that direct activation by impacts of hot particles cannot play any significant role. Therefore, all calculations of hypotheses based on the assumption of direct contact of explosive with the products of the reactions have no realistic physical basis, do not correspond to the physical state of combustion of actual explosives. The agreement of the conclusions from these hypotheses with the facts (where it does occur) cannot therefore be used as an indication of the correctness of the initial hypothesis, which is negated directly.

All of these factors have made it necessary to develop a theory of

combustion for the general case on the basis of modern concepts of the mechanism of chemical reactions and other physical processes, which go together to make up the process of combustion. The theory must give a physically correct picture of combustion, that is establish the sequence of chemical reactions during combustion, the reasons causing these reactions, the spatial distribution of the reactions, the distribution of material (the initial explosive and products of its conversion) and temperatures on both sides of the burning front.

It would be desirable to calculate the absolute values of combustion rate, based on the kinetic constance of the reactions and other properties of explosive and product of its conversion, and the dependence of the burning rate on pressure and on temperature. One natural requirement placed on the theory is that the predictions made on the basis of the theory should agree with the results of experiments and allow experimental results to be predicted.

III. Zel'dovich-Belyayev Theory of Combustion

The development of the theory of combustion of condensed explosives has been continued by Soviet investigators, in particular by Ya. B. Zel'dovich and A. F. Belyayev.

In 1938, Zel'dovich and Frank-Kamenetskiy [229] developed a theory of the stable burning of gases. Differential equations of the process were formulated and the course of the chemical reactions was analyzed quantitatively under conditions of variable temperature, changing as a result of the liberation of reaction heat, as well as with the influx of heat from layers already reacted and the transfer of heat to subsequent layers; at the same time, it was necessary to consider the movement of material by diffusion of reaction products in the direction of propagation of combustion and of initial material in the opposite direction.

In concluding the expressions for the combustion rate and its dependence on pressure and initial temperature, the assumption was made that the chemical reaction occurring during combustion proceeds almost entirely at a temperature near the maximum temperature of combustion. This assumption is correct for the most important case of strong dependence of reaction rate on temperature, typical for chemical kinetics, which occurs where $E \gg RT$.

Then in 1938 Belyayev turned his attention to the possibility of applying the theory of combustion of gases to the combustion of condensed explosives.

Many explosives have considerable volatility, and at moderate temperatures, when the reaction rate in the explosive rate is still slight, the rate of evaporation may be significant. This is determined by the fact that the heat of evaporation is much less than the activation energy and correspondingly the probability of evaporation of an explosive molecule on the surface is much greater than the probability of its decomposition². As a result of this, during rapid heating of the next thin layer of explosive in the process of combustion first evaporation of the explosive occurs, while the chemical reactions occur entirely in the vapor phase. For these conditions under which this affirmation is correct. (low external pressure, high volatility of explosive in combination with low rate constant of reaction in condensed phase), the combustion of the explosive can be looked upon simply as combustion of a gas (vapor) with the single difference that this gas is formed in the process of the combustion itself but evaporation of the condensed phase.

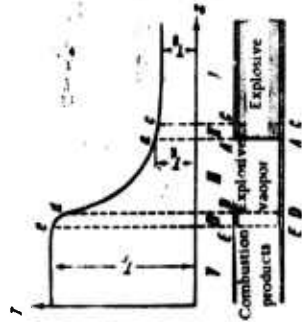


Figure 237. Diagram of distribution of temperature and course of reaction during burning of volatile explosives according to Belyayev.

Thus, the volatility was found to be the property of an explosive which has historically played an important role in the development of combustion theory.

Let us analyze the stable combustion of a volatile explosive in a tube of constant cross-section. The burning front is a thin zone, ECC (Figure 237) separating the cold initial explosive from the hot reaction products in which all chemical energy has been converted to thermal energy. The initial stage of the process in this case is propagation of the exothermic chemical reaction in the vapors. The heat transmitted from the reaction zone to the surface of the explosive causes it to evaporate at a rate determined by the rate of heat input. In the condensed phase, no chemical reactions occur, but rather only heating of the material from its initial temperature to the boiling point.

A comparison of the equations for thermal conductivity and diffusion show that the temperature and composition change simultaneously as a result of the chemical reaction. However, they change at the same time and in the zone where the chemical reaction does not occur: the temperature changes due to heat conductivity, the composition due to diffusion. In the particular case when the physical properties (molecular weight) of the participants in the reaction and the products of the reaction are similar, the kinetic theory of gases predicts that the values of diffusion coefficients and heat conductivity will be similar; then the relationship between temperature and composition along the front will be particularly simple, as if the reaction occurred adiabatically, without exchange of heat or of material with neighboring layers.

The distribution of temperature in space is shown on Figure 237: T_0 is the initial temperature of the explosive, T_k is the boiling point, T_g the maximum temperature achieved during combustion, occurs from left to right. The surface of the explosive at this moment in time is in the plane AA. The plane AA, separating the condensed explosive from explosive vapors (and since we are analyzing a stable process, the planes EE, DD and CC) move at rate u from left to right.

Let us analyze the process in the coordinate system moving together with the combustion front. In this system, plane AA does not move, but the explosive material moves into this plane from right to left at rate u , equal to the combustion rate. After being converted to vapors, the explosive will continue moving at a rate which is as many times greater as the density of the vapor is less than the density of the condensed explosive. As the vapors are heated, due to transmission of heat from neighboring layers and liberation of heat in the chemical reaction, the rate of movement will increase and, after the reaction is completed, reaches its maximum value. Here, since the process is stable, the mass velocity

² See p. 184.

(uo), i.e. the mass of material flowing through each zone per unit time, will remain the same.

A heated layer of explosive AACC is adjacent to plane AA. It is mathematically convenient to assume that the thickness of this layer AC is equal to the sector over which the temperature of the explosive decreases by e times, from which

$$\frac{T_a - T_0}{T_c - T_0} = e.$$

The vapors, moving from right to left, are heated by arrival of heat through thermal conductivity from the high temperature zone, and also due to the liberation of heat by the chemical reaction. With this, up to the bend point of the curve $T = f(x)$, the temperature gradient increases (in absolute value), while at the bend point the gradient passes through a maximum, then decreases, reaching zero at $T = T_0$. The heat flux balance changes correspondingly; to the right of the bend point, an element of volume receives more heat from the hot layers than it gives away to the cold layer; to the left of point d, an element of volume of the moving gases gives off more heat to the cold layers than it receives from the hot layers. This, naturally, does not mean that the heat reserve and temperature of an element of volume in this zone decrease, but rather increase due to the fact that as the temperature increases, the rate of liberation of heat by the chemical reactions also increases sharply.

The thermal balance equation for an element of volume in the reacting gas (vapor) located at a certain distance from plane AA can be written in the form

$$c_p \rho \frac{\partial T}{\partial t} = u c_p \rho \frac{\partial T}{\partial x} + \eta \frac{\partial^2 T}{\partial x^2} + F, \quad (4.10)$$

where c_p , ρ , η are the heat capacity at constant pressure, density and thermal conductivity of the gas respectively (it is assumed that the heat capacity and thermal conductivity are independent of temperature); F is the quantity of heat liberated by the reaction per unit volume per unit time (space velocity of heat liberation).

These equations show that a change in the thermal energy of an element of volume occurs: 1) as a result of movement of the gas with velocity u ; 2) due to "pure" thermal conductivity; 3) by liberation of heat as the chemical reaction occurs.

Since the fresh mixture always arrives from the colder portion of the volume, the first component of the right portion of the equation is always negative and decreases the quantity of heat at the given point.

The second curve in equation (4.10), equal to $\eta \frac{\partial^2 T}{\partial x^2}$ is the change in the thermal energy of an element of volume due to thermal conductivity and may be either greater or less than 0. At low temperatures (Figure 237) (sector cd-- the convexity of the curve turned downward) it is positive, while at high temperatures (sector de--convexity of the curve turned upward) it is negative.

The third term in equation (4.10) expresses the heat liberation resulting from the reaction, the rate of which depends on the concentration of reagents and on temperature.

Since we are concerned with a stable process and since it is assumed that the burning zone does not move, the distribution of temperature shown in Figure 237 does not change with time, since in expression (4.10) we can assume the ratio $\partial T / \partial t = 0$ and replace the partial derivatives with complete derivatives. Then this equation takes on the form

$$u c_p \rho \frac{\partial T}{\partial x} + \eta \frac{\partial^2 T}{\partial x^2} + F = 0. \quad (4.11)$$

If we analyze the zone where the temperature and rate of the chemical reaction, and consequently the heat liberation, are so small that heat liberation can be ignored, then assuming $F = 0$, the expression (4.11) can be written in the form

$$u c_p \rho \frac{\partial T}{\partial x} + \eta \frac{\partial^2 T}{\partial x^2} = 0. \quad (4.12)$$

Introducing the variable $\phi = dT/dx$, we produce

$$c_p \rho u \phi + \eta \frac{d\phi}{dx} = 0$$

or

$$\frac{d\phi}{\phi} = - \frac{c_p \rho u}{\eta} dx,$$

from which after integration we find

In order to solve this equation, Zel'dovich used the property of the Arrhenius law which states that the rate of a reaction depends strongly on temperature if, as is usually the case, the following condition is fulfilled:

$$E \gg RT. \quad (4.16)$$

The dependence of the rate of heat liberation in reactions of zero, first and second order on temperature for normal combustion conditions ($T_0 = 300^\circ\text{K}$; $T_g = 1900^\circ\text{K}$; $E = 50,000$ cal/mol) is presented in Figure 238.

When the condition of equation (4.15) is fulfilled, it can be considered that practically all the reaction occurs in a narrow temperature interval δ , i.e., between the temperatures $T_g - \delta$ and T_g , where

$$\delta \ll (T_g - T_0).$$

Since this interval is narrow, for the reaction zone the expenditure of heat for heating of the reacting material, i.e. we can assume

$$uc\rho \frac{dT}{dx} = 0.$$

Then the heat balance equation takes on the form

$$\eta \frac{dT}{dx} + F = 0. \quad (4.17)$$

Equation (4.17) means that in the reaction zone the heat carried away by thermal conductivity is equal to the heat liberated by the chemical reaction.

Using equation (4.17), we can determine the magnitude of the heat flux

$$\eta \frac{dT}{dx}.$$

Once more we introduce the variable $\phi = dT/dx$. Obviously,

$$\frac{dT}{dx} = \phi \frac{d\phi}{dT}.$$

Substituting this value into equation (4.17), we produce

$$\ln \phi = -\frac{C_1 \rho \eta x}{\eta} + C_2.$$

Since

$$\frac{C_1 \rho}{\eta} = \frac{1}{\chi},$$

where χ is the temperature conductivity coefficient,

$$\frac{dT}{dx} = e^{C_1} \cdot e^{-\eta x/\chi}. \quad (4.13)$$

from which

$$T = e^{C_1} \cdot \frac{\chi}{\eta} e^{-\eta x/\chi} + C_3. \quad (4.14)$$

The integration constant C_1 and C_2 can be defined from the condition that where $x = \infty$, $T = T_0$, while where $x = 0$, $T = T_k$; then $C_2 = T_0$ and

$$e^{C_1} = \frac{\eta}{\chi} (T_k - T_0).$$

Substituting these constants into expression (4.14), we produce the dependence of temperature T on distance x , measured from the plane with temperature T_k , in the form

$$T = T_0 + (T_k - T_0) e^{-\frac{\eta}{\chi} x}. \quad (4.15)$$

This relationship was first concluded for the theory of combustion by Michelson, and is correct for the zone in which liberation by the chemical reaction can be ignored.

In that area of temperature where heat liberation due to the reaction becomes important, term F in expression (4.11) is retained. This equation can be transformed as follows.

The rate of heat liberation F depends on the concentration of reacting material and temperature. Relating the concentration to the temperature, we can express the rate of the reaction and the rate of heat liberation as functions of temperature alone. This produces a second order equation, nonlinear due to the nonlinear dependence $F(T)$.

$$\eta \frac{d\eta}{dT} + F = 0$$

or

$$\eta Q d\eta = -F dT.$$

Integrating through the reaction zone, we produce

$$\eta \frac{\eta^2}{2} = \int_{T_r}^{T_c} -F dT \approx \int_{T_r}^{T_c} -F dT = \int_{T_r}^{T_c} F dT,$$

from which the temperature gradient at the boundary of the reaction zone is approximately equal to

$$\eta = - \sqrt{\frac{2}{\eta} \int_{T_r}^{T_c} F dT}$$

or

$$\eta Q = \eta \frac{dT}{dz} = - \sqrt{2\eta \int_{T_r}^{T_c} F dT}. \tag{4.18}$$

In expression (4.18), the integral of the rate of heat liberation with respect to temperature is taken through the entire area in which the reaction rate is other than zero. Due to the rapid decrease in reaction rate as the temperature drops, the principle component gives a comparatively narrow temperature interval near the combustion temperature.

Since the expenditure of heat to heating the reaction gas is being ignored, assuming that it is entirely accounted for by heat conductivity, the heat flux can be obviously set equal to the total quantity of heat liberated in the combustion zone per unit time, i.e. the product of the quantity of material burned by its heat value Q:

$$-\eta \frac{dT}{dz} = u_w Q.$$

Substituting this expression in the formula (4.18), we produce

$$u_w = \sqrt{\frac{2\eta}{Q} \int_{T_r}^{T_c} F dT}. \tag{4.19}$$

Since $F = wQ$, where w is the space velocity of the reaction,

$$u_w = \sqrt{\frac{2\eta}{Q} \int_{T_r}^{T_c} w dT}. \tag{4.20}$$

This expression shows that the rate of burning increases with increasing thermal conductivity and reaction rate at the combustion temperature. The rate of burning is proportional not to the first power, but to the square root of the reaction rate.

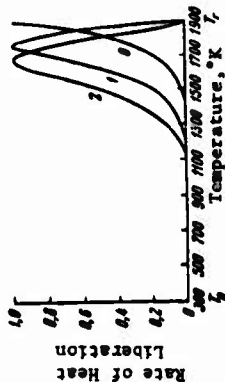


Figure 238. Space velocity of heat liberation during combustion as a function of temperature. The ordinate shows the rate in arbitrary units, the maximum value of rate for each of the curves being taken as one: 0, zero order reaction; 1, first order reaction; 2, second order reaction.

Substituting into formula (4.20) in place of F its expression through the concentration of reagents, which is proportional to the pressure in a power corresponding to the order of the reaction, and considering that by the time the maximum temperature has been achieved a portion of the material has already been reacted and that the material is slightly diluted by the reaction products, Zel'dovich produced the following expression for the mass rate of burning:

$$u_w = \sqrt{\frac{2\eta (RT_c)^{n+1}}{Q} (T_c - T_r)^{-n} w T_r}. \tag{4.21}$$

where u_m is the mass burning rate; E is the activation energy of the burning reaction; n is the order of the reaction; w_{T_r} is the reaction rate at the combustion temperature.

Formula (4.21) allows us to find the dependence of the combustion rate on the pressure and initial temperature. In this formula the pressure is included in concealed form, since the rate of reaction w_{T_r} in the gas phase is dependent on pressure.

Representing the product of all quantities included in equation (4.21) which are independent of pressure as B , we can write

$$u_m = B w_{T_r}^{1/n}.$$

As we know, the dependent of the rate of an n -th order gas phase reaction on pressure has the form

$$w_{T_r} = k p^n.$$

where k is the proportionality coefficient. From this

$$u = B_1 p^{n/n}, \quad (4.22)$$

where

$$B_1 = B k^{1/n}.$$

Thus, in a monomolecular reaction, the rate of burning should be proportional to the square root of pressure; with bimolecular reactions, the rate of burning should be proportional to the first power of pressure.

The physical sense of the influence of pressure is that at high pressure the reaction rate is higher and the zone in which it occurs (the high temperature zone) approaches the surface of the explosive more closely. The quantity of heat transmitted and, consequently, the quantity of explosive evaporated, increases in correspondence to the increase in the rate of the chemical reaction.

The dependence of the rate of burning on the initial temperature of the explosive is determined first of all by the dependence of the rate of the reaction on the burning temperature:

$$w_{T_r} \approx A e^{-E/RT_r}.$$

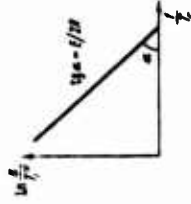


Figure 239. Dependence of burning rate of volatile explosives on combustion temperature according to Belyayev's theory.

The combustion temperature $T_g = T_0 + Q/c_p$; here c_p is the mean heat capacity of the combustion product at constant pressure. Thus, the higher the initial temperature, the higher the combustion temperature, the higher the rate of the reaction and correspondingly the higher the rate of combustion.

In formula (4.21), the combustion temperature in explicit or concealed form is included in a number of factors: $Q \sim T_g$, η increases with temperature, the concentration of the expression for reaction rate is inversely proportional to the temperature. The dependence on temperature of all factors included in expression (4.21) (except e^{-E/RT_g}) can be written in the form

$$f(T_g) = \gamma T_r^\gamma,$$

where γ includes all factors which do not depend on temperature.

The summary dependence of the burning rate on temperature can be expressed by the approximate relationship

$$u = \gamma T_r^\gamma e^{-E/RT_r}, \quad (4.23)$$

or

$$\frac{u}{T_g} = \gamma e^{-E/2RT_g}$$

logarithmizing which, we produce

$$\ln \frac{u}{T_g} = -E/2RT_g + \ln \gamma \quad (4.24)$$

Thus, in coordinates $\ln \frac{u}{T_g} - \frac{1}{T_g}$ the dependence of combustion rate of volatile explosives on the maximum combustion temperature should be shown by a straight line, the tangent of the inclination angle of which would be $E/2R$ (Figure 239).

The rate of the reaction in the gas phase, naturally, should not depend on the density of the powder, so that the mass velocity of burning should not change with a change in density. It follows from this that the linear rate of combustion should vary inversely proportionally to a change in density.

IV. Comparison of Experimental Data and Regularities with Conclusions of Vel'dovich-Belyayev Theory

The first explosive for which detailed comparison of theoretical data was performed was nitroglycol [230]. This comparison included a calculation of the absolute value of burning rate and its dependence on the initial temperature and pressure.

In calculating the rate, Belyayev used an approximate equation for the combustion reaction of nitroglycol, calculated from the composition of the combustion products in an atmosphere of nitrogen



The mean heat capacity of the combustion products with constant pressure $c_p = 0.34 \text{ cal/g-deg}$. From this, the increase in temperature during combustion of nitroglycol $\Delta T_g = T_g - T_0 = Q/c_p = 460/0.34 = 1350^\circ$, where 460 is the heat of combustion per gram of material. The maximum temperature $T_g = T_0 + \Delta T_g = 300 + 1350 = 1650^\circ C$. The heat conductivity coefficient of the combustion products at the maximum temperature $\eta = 2 \cdot 10^{-4} \text{ cal/cm-sec-deg}$.

Since the combustion reaction of nitroglycol is primarily a decomposition reaction, Belyayev considers this reaction to be monomolecular. However, if

calculations of the velocity are conducted using the expression for a first order reaction and if we use the values of activation energy and factor before the exponent produced for the slow thermal decomposition of this material [$k = 10^{14.3} \cdot \exp(-35,700/RT)$], the result of the calculation is approximately 200 times greater than the experimental value of combustion rate.³ Therefore, Belyayev, considering the experimentally established proportionality of the combustion rate to the first power of pressure (which corresponds to a second order leading reaction) assumed that the reaction rate of decomposition of nitroglycol at pressures near atmospheric was proportional to the number of collisions. With this assumption, in formula (4.21) he used $n = 1$, but in place of $n!$ he used $(n + 1)!$, i.e., 2.

The number of collisions $z = \sqrt{2} \pi \sigma^2 u$, where σ is the diameter of a molecule, u is its velocity, m is the number of molecules per cubic centimeter; the number of molecules reacting is twice as great as the number of collisions

$$w = \sqrt{6} \pi \sigma^2 \sqrt{\frac{RT}{M}} \frac{P^2 N^2}{R^2 T^2} \quad (4.26)$$

where M is the molecular weight of nitroglycol and N is the avogadro number.

The diameter of a molecule of nitroglycol is not directly known, and Belyayev assumed it to be equal to the diameter of the molecule of the esters of small molecular weight $\sigma = 5 \cdot 10^{-8} \text{ cm}$. Then we produce for the number of collisions

$$z = 4.13 \cdot 10^{10}$$

Considering that $T_g - T_0 = Q/c_p$, we produce

$$u_g = \sqrt{\frac{4RT_g}{M}} \frac{M}{2\pi \sigma^2 N} \quad (4.27)$$

Substituting the numerical values of the quantities included in this formula, we have

$$u = \sqrt{\frac{4 \cdot 2 \cdot 10^4 \cdot 27 (1650)^{0.35}}{(460)^2 \cdot 2^2}} \cdot \frac{152}{6 \cdot 10^8} \cdot 1.13 \cdot 10^{10} \cdot e^{-E/2RT_g} = \sqrt{\frac{1.12 \cdot 10^{11}}{E^2}} \cdot e^{-E/2RT_g} \text{ g/cm}^3 \cdot \text{sec}$$

³ See p. 184.

The experimental value of the combustion rate is $0.045 \text{ g/cm}^2 \text{ sec}$. This value of combustion rate is produced if we substitute the value of the activation energy produced with slow, low temperature decomposition of nitroglycol ($35,000 \text{ cal/mol}$) into formula (4.27).

On this basis, it was concluded that the theory of Zel'dovich indicates the correct, actually existing relationship between the kinetic constants of the material and the rate of propagation of combustion.

Even more convincing evidence in favor of this affirmation is given, according to Belyayev, by a comparison of the experimental and theoretical dependences of combustion rate on the initial temperature of the material.

From formula (4.23), considering the dependence of the coefficient of thermal conductivity and the number of collisions on temperature, we produce

$$u = 3 \sqrt{T_0^2} e^{-E/2RT_0} \quad (4.28)$$

or

$$\frac{u^2}{T_0^2} = \beta e^{-E/RT_0} \quad (4.29)$$

Logarithmizing, we have

$$\ln \frac{u^2}{T_0^2} = -\frac{E}{R} \frac{1}{T_0} + B. \quad (4.30)$$

Thus, laying out the inverse of the absolute combustion temperature on the abscissa, and the logarithm of the square of the velocity divided by the cube of the absolute combustion temperature on the ordinate, we should produce a straight line. Belyayev showed that this straight line is produced in actuality. Also, the tangent of the angle of inclination of this line should be E/R . Calculation of E from the tangent of the line actually produced indicates $E = 36,000-37,000 \text{ cal/mol}$, quite similar to the value produced from the equation for u -and to the value determined for slow thermal decomposition.

The method of determining E from the experimental temperature dependence of the rate of combustion, according to Belyayev, is most reliable, since this calculation does not include the rather indefinite quantities in the equation (i.e. the molecular diameter of nitroglycol, etc.)

The third possibility of testing the theory is presented by the dependence of combustion rate on pressure. For a first order reaction, the rate of which is proportional to the first power of pressure, the combustion rate should be proportional to the square root of pressure. Actually, for nitroglycol the rate of combustion is proportional to the pressure in the first power, or else slow thermal decomposition is a typical monomolecular reaction.

In order to resolve this contradiction, Belyayev suggests that the monomolecular reaction in those cases which occur at the combustion front is converted to a bimolecular reaction in the sense in which this occurs with all monomolecular reactions at very low pressures. As we know, the apparent dependence of the formation of activated molecules in monomolecular reactions on the number of collisions is a result of the fact that during collisions in addition to the activation, deactivation of active molecules also occur. If the lifetime of an active molecule is great in comparison to the time between collisions, a certain concentration of active molecules can occur which (and therefore also the total concentration of material) is proportional to the rate of the reaction.

Belyayev assumes that at the high temperatures at which the reaction occurs in the combustion front, the number of deactivating collisions is relatively small, and the monomolecular reaction therefore occurs at a rate proportional to the number of collisions, that is proportional to the square of pressure. This gives the proportionality of the combustion rate to pressure.

Subsequently, attempts to calculate the absolute value of burning rate were performed primarily for other explosives. For example, Arden and Powling [139] calculated the combustion rate of methyl nitrate vapors, assuming a combustion temperature corresponding to the experimentally determined composition of its products, and kinetic constants established for slow decomposition giving, however, different final products. This calculation indicated $u = 120 \text{ cm/sec}$ in place of 3.2 cm/sec determined experimentally.

A comparison of the theoretical and experimental influence of the initial temperature on the rate of combustion could not be performed, since it was found that the mass velocity of combustion did not increase with increasing initial temperature. Formally the conclusion would follow from this that either the combustion temperature is very high (which is not indicated by results of its measurement) or the activation energy of the leading reaction is very low. However, it is more probable that this anomaly is related to certain specific features in the course of the conversion, which leads in particular to the fact

that as the initial temperature is increased above 240°C the combustion ceases to propagate.

Gray [144] calculated the combustion rate of hydrazine, using the rate constant for slow decomposition (first order) ($E = 60$ kcal/mol) and produced $u = 30$ cm/sec in place of 200 cm/sec which was determined experimentally (rate calculated for vapors). Experiments on the dilution of vapors with various inert gases also showed relatively low activation energy (36 kcal/mol). Finally, the rate of combustion increases in proportion to the first power of pressure, which indicates the bimolecular nature of the leading reaction, whereas slow decomposition occurs according to the first order reaction rule.

All these data indicate that the primary reaction (or combination of reactions) which determines the course of slow decomposition cannot be accepted as the leading reaction during combustion.

The same conclusion is produced by a deeper comparison of the experimental and calculated temperature dependence of the combustion rate and rate of slow thermal decomposition for nitroglycol and a number of other explosives.

According to the theory for a first order reaction (for a second order reaction the difference is not too great),

$$u = \beta T_1^{1/2} e^{-E/RT_1} \quad (4.28)$$

From this, the temperature coefficient of the combustion rate—the ratio of rates of combustion at two temperatures T_2 and T_1

$$k = \frac{\beta T_2^{1/2} e^{-E/RT_2}}{\beta T_1^{1/2} e^{-E/RT_1}} = \left(\frac{T_2}{T_1} \right)^{1/2} e^{\frac{E(T_1 - T_2)}{RT_1 T_2}} \quad (4.31)$$

The higher the combustion temperature, the less k should be with a given E . Or, the greater k , the greater E should be at a given temperature.

Logarithmizing equation (4.31), we produce

$$\ln k = \frac{E}{2R} \frac{T_2 - T_1}{T_1 T_2} + \frac{3}{2} \ln \frac{T_2}{T_1} \quad (4.32)$$

or

$$\ln k = A \frac{E}{T_1 T_2} + \frac{3}{2} \ln \frac{T_2}{T_1} \quad (4.33)$$

Thus, the value of $\ln k$ is determined approximately by the ratio $E/T_1 T_2$, since T_2/T_1 is near 1, and the logarithm of 1 is 0. Thus,

$$\ln k \approx A \frac{E}{T_1 T_2} \quad (4.34)$$

$$\ln k \frac{T_1 T_2}{E} = A = \text{const.}$$

or

For many explosives on the basis of experimentally established compositions of the gaseous combustion products, the heat capacity of the explosive and the combustion temperature calculated on this basis, the values of activation energy calculated for various initial explosive temperatures and rate temperature factors according to equation (4.34) have been compared with the experimental values of E for slow thermal decomposition. These data are summarized in Table 38. In calculations for methyl nitrate, the heat capacity of 0.4 cal/g was used by analogy with nitroglycol and nitroglycerin. The combustion temperature was assumed higher for nitroglycol than that used by Belyayev. It was determined that in calculating this temperature he based himself on an approximate combustion equation, assuming in particular that all the nitrogen is liberated as NO. Actually, a small portion of the nitrogen is produced in elementary form. Consideration of the formation of nitrogen has a considerable influence on the results of the calculation. The heat of combustion of nitroglycol according to Belyayev's equation is equal to 460 cal/g, while with complete conversion of NO to N_2 this heat is about 1600 cal/g. Thus, it is natural that the conversion of even a small portion of the NO to N_2 increases the combustion temperature considerably.

Thus, for most of the explosives studied in this respect, including nitroglycol, which Belyayev first used to determine his theory, even satisfactory correspondence between the values of activation energy calculated on the basis of the temperature dependence of combustion rate and produced for slow thermal decomposition cannot be obtained. It should be emphasized that the value of E produced by calculating for combustion is sometimes so great that it is quite doubtful that this value can represent the activation energy of any of the reactions occurring combustion.

The reasons for this lack of correspondence between theory and experiments might be double; let us assume that the acceleration of combustion with an increase in the initial explosive temperature occurs not only by the mechanism

on which the theory is based, but also by another mechanism possibly not even connected with the kinetics of the reaction. Then the temperature factor for the rate of combustion will be artificially high which, in turn, as is clear from formula (4.34), leads to artificially high values of activation energy.

Table 38
Characteristics of Combustion of Certain Explosives

Explosive	Calculated combustion temperature (°K) with initial temperature		Ratio of combustion rates at 100 and 0°C	Heat capacity of explosive, cal/g	E _{cal}	Exp
	0°C	100°C				
Methyl nitrate	2003	2050 (at 50°C)	1.47 (at $\frac{w_{50}}{w_0}$)	0.4	121 000	39 500
Nitroglycerol Nitroglycerin	1804	1992	1.52	0.379	52 000	35 700
	2030	2129	1.82	0.356	91 000	50 000

The second possibility is that the assumption that the course of the combustion process is defined by a single reaction--the same reaction which occurs in relatively low temperature thermal decomposition and is characterized by the corresponding kinetic constants--is false.

The available experimental data give us no exhaustive answer as to which of these possible reasons determines the divergence between theory and experiment⁴. Apparently, both groups of reasons are valid.

The assumption that the leading reaction during combustion is the same as during slow thermal decomposition is not an organic element of Zel'dovich's theory. It can be assumed that the course of combustion is determined by some other reaction with a different activation energy, and this assumption can also be tested by a comparison with experimental data using the following methods [122].

The theory indicates a certain dependence of the temperature coefficient of the combustion rate on the combustion temperature (4.34), and consequently on the initial temperature of the explosive. As T_0 is increased, T_g also increases

⁴ See p. 184.

and consequently the combustion rate temperature coefficient should decrease, although only slightly (since the possible increase in T_0 is slight, and T_g is high). However, experience shows that for all explosives studied in this respect (Figures 169-171) the combustion rate temperature factor not only did not decrease, but clearly increases as the initial temperature of the explosive is increased. This increase is generally expressed more weakly at higher pressures⁵, i.e. at 50 atm in comparison with 25 or 1 atm.

Another possibility for testing the theory is given by establishing the influence of pressure on the temperature dependence of the combustion rate. The theory does not predict this influence. However, experience shows that it does appear (see Table 26). For all explosives studied, the temperature factor decreases as pressure is increased; for certain explosives, for example hexogen, this influence is relatively weak; with a change from 1 to 50 atm, k decreases from 1.25 to 1.14; for other materials the effect is considerably stronger, for example for tetryl from 1.35 at 12 atm to 1.17 at 50 atm.

This last dependence contradicts the conception according to which the leading role is one reaction independent of the other reactions which occurs at a constant temperature independent of pressure and equal to $T_0 + Q/c$, where Q is the thermal effect, and c is the mean heat capacity of the products. However, if we consider the undeniably established multistaged nature of the gas phase conversion, this dependence can be explained by assuming that as the pressure increases the zone in which the later exothermic stage occurs approaches the zone of the leading reaction and slightly increases the temperature of this leading reaction, making it less "sensitive" to the initial temperature. If increased pressure and initial temperature both act in a similar manner, this can be explained by an increase in the temperature coefficient as the temperature is increased. A decrease in the growth of the temperature coefficient with initial temperature at high pressure can also be explained. If the pressure increases the effective temperature of the leading reaction, it becomes less sensitive to other influences which produce the same effect. The relatively weak appearance of both of these influences for "hotter" materials such as hexogen in comparison with tetryl would also be understandable.

⁵ See p. 184.

would give artificially high values of activation energy. In order to determine the reasonableness of this possibility, G. V. Oranskaya performed a determination of decomposition of gaseous combustion products of nitroglycerol and pyroxylin No. 1 at room temperature and at 95°C. It was established that a slight change in gas composition apparently does occur with increasing initial temperature, but that it is quite slight and insufficient to explain the very high activation energy.

Experiments have shown that the rate of combustion of liquid explosives depends essentially on the viscosity of the liquid. A considerable increase of the latter (by gelatinizing a small quantity of the high polymer) decreases the rate of combustion of nitroglycerol by one-fifth, of nitroglycerin by one-third. The decrease in the rate of combustion with increasing explosive viscosity is observed at low (room) temperatures, while at high temperatures (about 100°C) no decrease in combustion rate is observed, probably because the viscosity of the gelatin at high temperatures is decreased sharply.

The influence of viscosity on the rate of combustion of an explosive can be related to the fact that the liquid at the surface boundary with the gas boiled during combustion in the usual sense of this word or that a phenomenon similar to boiling is produced, as a result of the separation of bubbles of dissolved gases. This bubbling of the liquid, possibly causing a spray of the liquid to be carried away with the gases, creates the necessary microrelief of the surface and reinforces heat exchange of gases with liquids, as a result of which the rate of combustion increases. Obviously, the intensity of the phenomenon should depend on the viscosity, which explains the influence of viscosity. However, with this mechanism of the influence of viscosity on combustion rate, it is clear that the temperature coefficient of combustion rate, at least for liquids with high viscosity, and viscosity strongly dependent on temperature, may be quite high due to this effect.

It should be added that for relatively rapidly burning liquids a distortion of the surface is possible and an increase of the rate may occur due to the Landau effect (see below p. 303 [page 303 of original text, not requested for translation]). For example, it cannot be excluded that the great acceleration of the burning of methyl nitrate with temperature results from this factor.

⁶ See p. 184.

Let us analyze the dependence of the rate of combustion on pressure. We noted above that this dependence was constant, established experimentally. For the simplest case of volatile explosives, the combustion rate is determined by the expression $u = A + Bp$, where term A is very small, and apparently related to side factors, so that the rate of combustion can be considered proportional to the pressure in the first power. According to the theory, this means that the leading reaction is bimolecular. The assumption of Belyayev that as the pressure is increased a transition from the dependent $u(p)$, corresponding to the bimolecular nature of the leading reaction ($u \sim p$) to a dependence corresponding to monomolecular reaction flow ($u \sim p^{1/2}$) has not been confirmed. For all solid, relatively volatile organic nitrates and nitrocompounds studied, the rate of combustion throughout the entire broad investigated pressure interval (up to 1,000 atm) increases approximately proportionally to pressure. At the same time, slow thermal decomposition of all these explosives is a first order reaction.

The simplest explanation of the experimental dependence of rate of combustion on pressure is that the leading reaction is a bimolecular reaction, more precisely one occurring through double collisions. This also leads us to the conclusion that this leading reaction is not the reaction determining the rate of monomolecular decomposition.

Let us analyze in more detail the possible explanations of the experimental dependences of combustion rate on temperature and the probable diagram of the course of the combustion process.

First of all, let us pause on one trivial possible explanation of the divergence of theory and experiment. The combustion of all explosives studied at low pressures near atmospheric pressure leads, as we indicated above, to incomplete conversion products. At high pressures, the completeness of combustion increases and, finally, beginning at a certain pressure, we produce a composition of gaseous combustion products corresponding to thermodynamic equilibrium. It might be assumed then increasing the initial temperature of the explosive would have a similar effect and that with increased initial temperatures decomposition of the combustion products would change in the direction of increasing the completeness of combustion and the temperature of the gaseous combustion products. This situation, if it does occur, could yield an additional increase in the rate of combustion, failure to consider which

In addition to the physical reasons indicated, an influence of viscosity more closely related to the kinetics of the chemical process of combustion is possible. When such explosives as organic nitrates and nitro-compounds burn, the decomposition of molecules does not occur immediately; first of all, primarily gaseous compounds of nitrogen with oxygen split off, particularly in NO_2 , which is relatively rapidly reduced to NO . As a result of this, the surface layer of liquid becomes poorer in the oxidizer, which has been replaced by diffusion from the deeper layers. The rate of diffusion is less, the higher the viscosity of the liquid. An increase in the viscosity also hinders convective mixing, which may play a role at low burning rates. The fact that an increase in viscosity influences the process most strongly with relatively rapidly burning liquids argues for this explanation.

When we analyze the possible reasons for the disruption of "normal" dependence of the combustion rate on the initial temperature in the direction of the production of an increased temperature coefficient, we assume the correctness of Belyayev's assumption that the combustion rate is determined by the rate of the monomolecular reaction, which is identical to the reaction occurring during slow thermal decomposition.

This assumption, however, has no serious foundations; the principal argument in its favor is the correspondence of the activation energies which, it has been found, were produced by Belyayev. If the chemical conversion during combustion occurred in one stage, naturally, this reaction would be the determining reaction, as follows from combustion theory.

However, it is almost certain that for all the explosives analyzed this is not the case and that even those products of incomplete combustion which are produced at atmospheric pressure are a result of two or more reactions. They are serious, although indirect, reasons to assume that, for example, in the combustion of nitroesters and nitro-compounds the primary reaction is endothermic or weakly exothermic splitting of nitrogen dioxide, which then reacts with the other intermediate decomposition products, possibly also with the initial material.

It is quite possible and probable that this primary reaction determines the rate of slow homogeneous thermal decomposition of the explosives. Although during this decomposition secondary reactions also occur, generally in the same direction apparently as during combustion (judging from the similarity of the

reaction products), the total rate of decomposition may be determined by the slowest of the subsequent reactions alone. Whether this reaction is endothermic or exothermic under slow decomposition conditions is not important, since the reaction occurs at constant temperature maintained by heat exchange with the external medium. Judging from the fact that the end products of the reaction under ordinary conditions contain no nitrogen dioxide, it must be concluded that it is the primary reaction (leading to its formation) which is the slowest.

The thermal effect of the reaction during combustion has a quite different significance. In this case, the temperature at which the reaction occurs and the rate of the reaction are determined by the positive thermal effect of the reaction. Therefore, the primary endothermic reaction also can have little effect on the combustion rate⁷, like the endothermic physical process of evaporation, the latent heat of which is not included in the expression for combustion rate produced by Zel'dovich.

The rate of combustion is determined by the course of the reaction (or reactions) in which the principal portion of the thermal effect of combustion is released. The rate of the endothermic primary reaction is automatically established in correspondence to the rate of the leading reaction. If the rate constant of the primary reaction is great, the zone of maximum temperature is located far from the zone of the primary reaction, and the temperature in this latter zone is relatively low, so that the rate of both reactions is identical, a necessary condition for stable processes.

If we imagine that the rate of the primary reaction has decreased and begun to extend into the depth of the material more slowly than the leading reaction, the front of the leading reaction will approach the zone of the primary reaction, and the temperature in this zone will increase until its propagation rate becomes equal to the propagation rate of the leading reaction.

Thus, if chemical conversion during combustion is a set of two successive reactions--one endothermic and one exothermic (occurring "independently" due to the heat liberated), the course of the endothermic primary reaction, like that of endothermic evaporation, will be forced and the rate of these processes will be automatically regulated by the leading reaction.

Matters are more complex if several successive exothermic reactions occur during combustion. Here, obviously, the leading reaction is that which under the conditions under which it occurs (temperature and pressure) propagates

at the highest rate. If, for example, this is the second of two successive exothermic reactions, it will "press" the first reaction, which occurs more slowly; due to the transfer of heat, the rate of the first reaction will increase to the rate of the more rapidly propagating reaction. If the second exothermic reaction occurs more slowly, it will lag behind the flame front and may have no direct influence on the course of combustion.

However, we must consider that as the combustion temperature changes (by changing the initial temperature of the explosive) or the pressure changes, the relationship between reaction rate changes and the roles of the reactions may be interchanged. It is necessary also to keep in mind the possible influence of heat losses, particularly important for slowly occurring reactions. As an example, we indicate the combustion of nitroglycerol at atmospheric pressure. The principal compound nitrogen is NO, of carbon--CO, i.e. gases capable of interacting; however, this interaction under ordinary experimental conditions practically does not occur, obviously because the decrease in temperature resulting from heat losses exceeds the heat influx, which is low due to the low rate of the reaction between CO and NO. As the pressure is increased, due to the decrease in heat losses⁸ a second flame appears in which the nitric oxide is reduced to nitrogen with considerable thermal effect. This flame is located at a large (1-2 cm) distance from the surface of the liquid and can have no effect by thermal conductivity on the rate of combustion and in actuality does not influence this rate, which is indicated by the absence of any notable change in the rate as this flame appears. However, as the pressure is increased further, we should expect the second flame to approach the surface of the liquid, which gives us reason to believe that it is this final reaction which is the leading reaction for nitroesters at high pressures.

At low pressures, the leading reaction is another reaction, possibly leading to products which are the final products at these pressures. The argument in favor of this assumption is the similarity of the order of magnitude of the experimental values of combustion rate and the theoretically calculated combustion rate values, based on the combustion temperature corresponding to the final gas composition at atmospheric pressure. The fact that this agreement is produced with a reasonable value of activation energy for

⁸ See p. 185.

slow decomposition in those cases when this similarity is genuine⁹ indicates nothing in itself, particularly since the calculated value of combustion rate is rather insensitive even to considerable changes in the value of E and T used for calculation¹⁰.

If the agreement between calculated and experimental values of combustion rate is produced for any one of the nitroesters, it will be observed for all other nitroesters, since the rate of combustion of these products (at atmospheric pressure) differs, generally speaking, little (approximately from 0.015 cm/sec for diglycoldinitrate to 0.11 cm/sec for methylnitrate), while the combustion temperatures of these nitroesters for which there is one CNO₂ group for each carbon atom are also similar. It is possible that the leading reaction is monotypic, as apparently the primary reactions are monotypic. Even for volatile explosives of other classes burning according to the mechanism analyzed, we cannot expect combustion rates many times greater than that of methylnitrate for example, since this would indicate unrealistically high combustion heats or very low activation energies, which are also unrealistic, particularly in combination with the first condition. Thus, the combustion rate of volatile explosives is limited, generally speaking, to comparatively low upper limits.

However (regardless of these considerations), the agreement within the limits of a few orders of magnitude between the theoretical calculation of the absolute value of combustion rate for many explosives with calculations not including any empirical constants, and the experimental values can be considered a sufficient indication of the basic correctness of the theory. It is the task of future investigations to establish the reactions which lead the process, their kinetic characteristics and the temperatures at which they occur.

One interesting question is that of the pressure area in which the leading role is transferred from reactions forming NO to reactions leading to its reduction. It is usually assumed that this transition occurs at pressures of about 100 atm; the principal consideration apparently is the fact that at about this pressure the secondary flame approaches the primary flame so closely that the dark zone between them becomes unnoticeable. However, there are both experimental and logical reasons to assume that actually this transition occurs at much higher temperatures. Thus, nitroglycerol and nitroglycerin are quite

^{9, 10} See p. 185.

similar energetically; at the same time nitroglycerin (at atmospheric pressure) burns four times more slowly than nitroglycerin, which can be attributed to differences both in effective combustion temperatures and in the kinetics of the reactions which lead at low pressures. It is obvious, however, that in the terminal stage of combustion both of these considerations disappear, since we are now concerned primarily with the interaction of CO and H₂ with NO, while the thermal effect of the reaction is identical. Therefore, in those places where the leading role is transferred to the final stage, the rate of combustion should be identical. However, experience has shown that even at 1,000 atm nitroglycerin burns 1.4 times more slowly than nitroglycerin (both nitroesters were gelatinized with nitrocellulose in order to prevent the transition of normal combustion to the excited regime). It can be concluded from this that even at 1,000 atm the leading reaction is basically the same which fills this role at low pressures. At the same time when these two nitroesters are burned in their ordinary liquid state with a turbulent regime, even at 100 atm the rate of combustion is similar; under these conditions, the zonal distribution of temperature is eliminated by turbulent mixing and the rate of evaporation is determined by the final combustion temperature.

For many explosives (for example PETN, trotyl, picric acid), the combustion rate throughout the entire interval which has been studied (up to 1,000 atm) increases in proportion to pressure, the proportionality coefficient remaining unchanged. The simplicity in this dependence and the identical nature for different explosives allows us to believe that it is not by chance, and does not represent the result of condensation of various influences, but rather is the result of the bimolecular nature of the leading reaction, the characteristics of which do not change within this pressure interval. Since at low pressures, when the terminal stage of the reaction generally does not occur, the leading reaction can only be the initial or one of the intermediate stages, we should conclude that this stage retains its leading role at 1,000 atm.

The experimental results are not unexpected. At low pressure, the final stage occurs more slowly than the leading stage, and correspondingly the zone through which it occurs is far from the hot surface. Increased pressure accelerates both stages. The leading stage, judging from the dependence $u(p)$, is bimolecular; it is difficult to assume that the final stage is a reaction of higher order. This means that the influence of pressure on both stages should be identical. If an increase in pressure still causes the zone of the final

reaction to approach the zone of the leading reaction, this occurs partially due to the fact that with increases in gas density the heat losses¹¹ are decreased and flaming of the products of the final reaction occurs earlier.

Another reason for the acceleration of both stages might be the increase in the temperature at which they occur for the first reaction due to the receipt of heat from the zone of the second reaction, and for the second reaction due to the decrease in heat losses. However, the decrease in heat losses can hardly increase the final temperature strongly, particularly since it is so high. At the same time, the increase in temperature of the leading reaction, which is relatively low, should strongly influence its rate¹² and, as a result of this, should cause the zone of the final reaction to shift. Thus, on the basis of the relationships which obtain for combustion under low pressures, there is no reason to expect a rapid transition of the leading role to the final reaction as the pressure is increased.

The fact that the temperature of the end products is not necessarily the temperature at which the leading reaction occurs is shown by simple experimentation. If we calculate the combustion temperature of nitroglycerin by gas analysis, we can produce a sharp jump in burning rate at about 15 atm, which is not actually observed. Also, the usage in our calculations of a temperature on the order of 4,000°, corresponding to the final (and in this place complete) decomposition at a pressure of 15 atm, sharply elevated values of combustion rate would be produced.

Nonfulfillment of the dependence of combustion rate on pressure corresponding to monomolecular flow of the reaction can also be explained if we assume that one of the secondary reactions is the leading reaction. This reaction between molecular fragments, for example between NO₂ and formaldehyde or a radical, should naturally occur upon collision of the corresponding particles; the number of collisions is proportional to the product of the concentrations; i.e. the square of pressure. Although this fact does not exclude the possibility that the chemical conversion will follow the first order reaction rule, if we consider the simplicity of the fragments this possibility is not probable. If in our calculations we replace the reaction of decomposition of a nitroester molecule with the reaction between the products of its primary decomposition, almost no

^{11, 12} See p. 185.

change in the numerical result of the calculation will be seen.

Thus, the Zel'dovich-Belyayev theory in our interpretation is quite natural and, without changing the principle ideas of the theory, we can correct it in correspondence with the fact established for combustion of volatile explosives.

V. Mechanism of Combustion of Nonvolatile Explosives

The principal distinction in the combustion of nonvolatile explosives is that when combustion is performed in the condensed phase we can achieve relatively high temperatures at which the rate of chemical conversion cannot be ignored, as was assumed in our analysis of combustion of volatile explosives when the temperature of the condensed phase at the hot surface could not be above the boiling point.

Experience has shown that the combustion of nonvolatile organic secondary (high polymer nitrate) explosives shows no differences in principle from the combustion of volatile explosives as concerns the dependence of combustion rate on pressure. In just the same way, a change in the dependence of $u(p)$ is observed with a significant increase in pressure, when the volatile explosives "lose" their volatility. The most noticeable different of this dependence for nonvolatile explosives is the presence in the extended linear dependence $u = A + Bp$ of a significant term A , which does not depend on pressure and is 2-4 times greater than B (using the ordinary unit for expression of mass velocity and pressure). This means that the combustion rate at atmospheric pressure is great in comparison to volatile materials of similar chemical structure and combustion heat. The most probable explanation of this difference, as was suggested by Marzouk is that this term shows the course of the exothermic reaction in the condensed phase and the influx of heat from it to the powder layer entering the combustion process¹³. This heat is transmitted through the condensed phase by heat conductivity, which is great (in comparison to the thermal conductivity of the gas) and therefore is more completely used for propagation of the combustion process than the thermal conductivity of the gas phase reactions, the zone of which is separated from the surface of the explosive by a more (at low pressures) or less (at high pressures) thick layer of gaseous products of the first stage of chemical conversion.

¹³ See p. 185.

Another explanation of the presence of term A , considering it to be an apparent term, was suggested by Belyayev [231]. He suggested that in the combustion of nonvolatile explosives the principal reaction penetrates into the pores and occurs in them under slightly increased pressure P_c , which gives term A in the equation. The argument in favor of this explanation is the constancy of the calculated pressure increase Δp in experiments with fulminate of mercury at various temperatures. The absolute value of the suggested pressure increase for fulminate of mercury is not great--300 mm, while for trinitrotriazidobenzene it is 150 mm. However, when other explosives are burned, for example pyroxylin No. 1, colloxylin, much greater Δp would have to be assumed (2.2 and 4.5 atm respectively), while for nitroglycerin powder the increase would be even greater--100-150 atm, which is clearly incorrect.

Another difference in nonvolatile explosives (concretely nitrocellulose) from the volatile low molecular nitroesters is the relatively high temperature coefficient of burning rate, which increases essentially with an increase in the initial temperature. At the same time, the temperature coefficient depends on density, increasing as it increases. This last factor cannot be explained from the point of view of the leading role of gas phase chemical conversion and clearly indicates the essential role of processes in the condensed phase.

The influence of inert impurities on the combustion of a nonvolatile explosive investigated in this respect--pyroxylin No. 1--is also unique. A particularly sharp decrease in combustion rate for each percent of added water, in contrast to the theory of gas phase combustion, is observed (Figure 240) at first at small content; this damping occurs at a rate amounting to less than one-half of the rate of combustion of the nondiluted material. The curve expressing the change in rate of combustion as a function of water content is similar to the curve expressing the change in combustion rate with changing initial temperature. In this case (according to calculation) the decrease in combustion temperature as the initial temperature is decreased from 100 to 0°C (but not below) leads to the same decrease in combustion rate as a decrease in the combustion temperature by adding the corresponding quantities of water. Thus, the influence of water can be looked upon actually as simple thermal dilution.



Figure 240. Influence of moisture content on combustion rate of pyroxylin No. 1 at various temperatures (in °C): 1, 95; 2, 20.

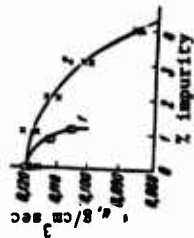


Figure 241. Influence of inert impurities on rate of combustion of gelatinized nitroglycerin (97:3). 1, H_2O ; 2, $(NH_4)_2CO_3$.

The problem of the quantitative correspondence of the theory of both of these cases of the decrease in combustion rate is interesting. This interest is increased by the fact that a similar study of the influence of inert impurities (ammonium carbonate, water) on the rate of combustion of a volatile material (slightly gelatinized nitroglycerin) gave a quantitatively quite different dependence of combustion rate on impurities content (Figure 241). With the highest content (4%) of the additive $(NH_4)_2CO_3$ at which combustion was observed, its rate was three-fourths of the rate of combustion of the nondiluted material.

According to Zel'dovich's theory, as we know, the ratio of maximum and minimum possible combustion rates at a given pressure should not exceed \sqrt{e} ; with pyroxylin, this ratio is clearly greater.

It should be stated that the difference between the volatile and nonvolatile explosives is arbitrary to a certain extent. As the pressure increases, the boiling point of the volatile explosives increases¹⁴ and correspondingly at a few tens of atmospheres all ordinary explosives have a boiling point much higher than the flash point, which can be looked upon as a sort of arbitrary criterion for volatility of an explosive. On the other hand, Zel'dovich has shown that if the decomposition of a nonvolatile explosive (its conversion to gaseous products) occurs endothermically or with liberation of only a small portion of the heat of complete conversion, while subsequent exothermic reactions occur in the gas phase, the combustion of this nonvolatile explosive can be quantitatively

¹⁴ See p. 185.

looked upon as combustion of a volatile explosive; however, this is not the only possibility during combustion of nonvolatile explosives. If the reaction of gasification of the condensed phase is sufficiently exothermic, it may become the leading reaction. In particular, if the pressure under which the burning of volatile explosives is increased, the boiling point will increase and correspondingly the rate of conversion and heat liberation in the condensed phase will increase. At a certain pressure, particularly considering that the density (concentration) of the condensed phase is 3 orders higher than that of the gas phase, the velocity of the thermal wave in the condensed phase may become comparable to or even greater than the velocity of the wave created by the gas phase reaction; then, the rate of combustion will be determined by the rate of mixing of the zone of liquid in which the liquid is heated to the boiling point due to the reaction occurring within it.

For this case, Zel'dovich analyzed (ignoring the change in concentration of the reaction molecules when heated to a temperature near T_k) the rate of propagation¹⁵

$$u = \frac{1}{\rho_l(T_k - T_0)} \sqrt{\frac{2\eta Q B e^{-E/RT_k}}{E}} \quad (4.35)$$

where ρ , c_p , η are the density, heat capacity and heat conductivity coefficient of the liquid; T_k is the boiling point of the liquid; Q is the heat of the reaction in the condensed phase (cal/cm³); B is the pre-exponential factor; E is the activation energy.

As in the case of combustion in which the leading reaction is gas phase conversion, the theory can be compared with experimental information by calculating the dependence of combustion rate on initial temperature and its absolute value. An estimate using the expression for the dependence of combustion rate on pressure is also possible, although this estimate, due to the dependence of latent heat of evaporation on pressure, not considered by expression (4.35), can be extended only to the area of pressure where the change in λ is small.

Many points in the combustion of smokeless powders at low pressures agree much better with the conclusions following from the assumption that the leading reaction in this case is the reaction in the condensed phase. Belyayev [232]

¹⁵ See p. 186.

calculated the rate of combustion of pyroxylin powder at extremely low pressures at which it is independent of pressure and correspondingly is determined only by reactions in the condensed phase. This calculation was performed using Zel'dovich's formula for the velocity of the heat wave resulting from the reaction in the condensed phase and heating the material to a certain limiting temperature (in the case of volatile materials, eq. 4.36 to the boiling point).

$$u = \frac{1}{\rho_0(T_0 - T_b)} \sqrt{\frac{2\eta Q \rho_0 c - E R T_0}{R}} \quad (4.36)$$

Assuming, according to the data of other investigators, $\rho = 1.6 \text{ g/cm}^3$, $c = 0.29 \text{ kcal/deg}$, $\eta = 5.5 \cdot 10^{-4} \text{ cal/cm}^2 \cdot \text{sec} \cdot \text{deg}$, $Q = 80 \text{ cal/g}$, $R = 10^{17} \text{ sec}^{-1}$, $E = 44,600 \text{ cal/mol}$, $T_b = 573^\circ \text{K}$ (300°C), $T_0 = 363^\circ \text{K}$, Belyayev produced $u = 3.4 \cdot 10^{-2} \text{ cm/sec}$, only one-half the value established earlier by experiment. Considering possible errors in the values of a number of quantities included in formula (4.36), the agreement of the result of calculation with the experimental values should be considered satisfactory.

The dependence of combustion rate on initial temperature follows directly from formula (4.35). Representing by u the terms of the expression which do not depend on T_0 , we produce

$$u_0 = \frac{u}{T_0 - T_b} \quad (4.37)$$

and for the temperature coefficient

$$k = \frac{T_0 - T_1}{T_0 - T_2}$$

where $T_1 - T_2$ are the initial temperatures of the explosive.

It follows from formula (4.37) that

1) The dependence of the combustion rate on initial temperature should be determined by the change in the quantity of heat necessary to heat the condensed phase from the initial temperature to the boiling point when T_0 is changed. In the general case, the higher T_b , the weaker this dependence should be;

2) As the pressure is increased, the temperature dependence of burning rate should decrease in correspondence with the increase in T_b .

3) As the initial temperature increases, the combustion rate should increase more strongly, the higher T_0 , i.e. the temperature factor for combustion rate calculated for successive equal intervals of change of T_0 should increase with increasing T_0 .

In the coordinates $1/u - T_0$, the dependence of combustion rate on initial temperature should be illustrated by a straight line.

These results, with the exception of the second one, differ formally very little from those which follow from the hypothesis of Michelson and Mallard-LeChatelier, but in contrast to them they follow from the conceptions which consider the physical-chemical and kinetic characteristics of the material.

Until recent times, the dependence of $u(T_0)$ was determined for most volatile and nonvolatile explosives studied only at atmospheric or near atmospheric pressures. Only for nitroglycerin powder has this definition been extended to moderately high pressures, and it has been established that the dependence $u(T_0)$ weakens with increasing pressure. For atmospheric pressure, the rate increases with T_0 not linearly, but more rapidly. This increase is expressed in the coordinates $1/u - T_0$ by a straight line. The point of intersection of this straight line with the abscissa gives us an intelligent value for critical temperature, somewhat higher than the values produced by standard determination of the flash point.

However, the dependence $u(T_0)$ for nitroglycerol, as was shown by Belyayev [230], can be described by the expression

$$u = T_0 e^{-E/RT_0} \quad (4.38)$$

which follows from gas phase combustion, and it is impossible to explain this by illustrating the reality of the existence of any given mechanism.

This possibility explains the difference of initial temperature and pressure on the combustion rate temperature coefficient.

According to gas phase theory, as was noted, this coefficient should decrease slightly with increasing temperature; with combustion, when the leading reaction occurs in the condensed phase, it should increase. Actually, the temperature coefficient for all the explosives studied increases, particularly strongly for a clearly nonvolatile explosive—nitrocellulose; this dependence is also

influenced by increased pressure, which decreases at "hot" (hexogen) or relatively volatile (i.e. trinitrobenzene) explosives show a lower dependence of temperature coefficient on temperature.

Thus, the set of all dependence is established in studying the influence of initial temperature on combustion rate agrees qualitatively with the assumption of the leading role of the exothermic reaction in the gas phase.

This conclusion agrees with the results of attempts to detect chemical conversion in the condensed phase by interrupting combustion.

Cessation of combustion was achieved either by performing the combustion (at atmospheric pressure) in conical tubes or by pouring a cooling liquid (liquid nitrogen) over the charge burning in the tube. The presence of thermal decomposition in the layer adjacent to the surface was determined by the decrease in the melting point of the explosive. In all cases, a significant decrease in the melting point was observed, the greatest for tetryl (25°C) and the least for trotyl (1°C).

However, we must emphasize again that no qualitative difference was observed in the dependence $u(T_0)$ between volatile and nonvolatile explosives. Furthermore, we have seen that the established influence of pressure and initial temperature can be explained from the point of view of gas phase combustion. In this case, however, certain assumptions must be made which have not been directly tested by experimentation, which is not required if we assume that the process occurs in the condensed phase.

As yet, we have analyzed only the dependence of combustion rate on initial temperature, which produces a reaction in the condensed phase. However, it also allows us to estimate the dependence $u(p)$. The boiling point of the explosive depends on the pressure $\ln p = -(A/RT_1) + \ln A$. Using this relationship, we produce

$$u_a = \beta p^\gamma = \beta p^{E^*A} \tag{4.39}$$

where

$$\beta = \frac{A^* T_a}{c_p (T_a - T_0)} \sqrt{\frac{R}{2\eta Q E}}$$

16 See p. 186.

Table 39 shows values of v produced by experimentation (v_1) and by calculation using formula (4.39) and (v_2) and considering the change in $T_k/(T_k - T_0)$ with pressure (v_3).

Table 39
Experimental and Calculated Exponents of Pressure in the Expression $u = Bp^v$ in the Interval 1-50 atm

Explosive	"	"	"
Hexogen	0.85	0.81	0.81
PETN	1.00	0.87	0.845
Tetryl	0.69	0.74	0.73

The agreement is quite satisfactory, particularly if we consider the insufficient reliability of λ for high boiling explosives. In addition to this, when the pressure is increased λ is decreased which should lead to an increase of v . It is possible that this influence is weakened as a result of the decrease in time which the explosive spends in the heated state and the decrease in chemical self-acceleration of the reaction.

Formula (4.35a) allows us to calculate the absolute values of combustion rate of these explosives; the results of calculation presented in Table 40 show that the experimental values differ from the calculated values by not more than four times. Considering the quite approximate nature of many of the quantities included in expression (4.35a), this agreement must be considered quite satisfactory.

Thus, in this case as well the usage of the expression for the leading reaction in the condensed phase gives results which are closer to the experimental results than the formula for the gas phase reaction, particularly when the calculation is performed using the rate constants for thermal decomposition. It should be added that the calculation for the condensed phase is closer to the experimental data, since first of all the performance of the reaction in the liquid phase corresponds more closely to the conditions of slow decomposition and secondly the difference in temperatures is much less than if the data of slow decomposition are extrapolated to the maximum combustion temperature. Therefore as a whole the theory of the leading reaction in the condensed phase is no worse, and probably even better in its description of the experimental data produced for fusible secondary explosives as concerns the absolute value of velocity, its dependence on initial temperature and the pressure.

It is possible that there is no particular reason to set these conceptions in opposition; we can imagine that exothermic reactions occur and interact both in the gas and in the condensed phases. When the combustion conditions change, the specific weight of each of these reactions changes, so that combustion takes on features characteristic for one of the regimes to some extent. The quantitative conclusions concerning the relationship of the two reactions can apparently be produced only by determining the temperature profile in combustion and calculating the specific weight of each reaction on this basis.

There is another possibility limiting the development of the reaction in the condensed phase for nonvolatile explosives, which is similar to some extent to evaporation.

This possibility consists of dispersion of a considerable portion of the solid explosive during combustion. In general, the form of the dispersion is related to a combination of three specifics in the chemical conversion of explosives during combustion--the transition of the condensed explosive to gases with considerably lower density, with the chemical conversion during combustion occurring not only on the surface but also to a considerable depth in the heated layer of the condensed phase and with unevenness of chemical conversion in space.

The first two specific features are also characteristic of volatile, fusible explosives, but the temperature limitation of the surface and heated layers by the endothermic process of evaporation, the possibility of equalization of local heating in concentrations of conversion products by diffusion and convection makes the possibility of dispersion more difficult, and it is observed only under certain specific conditions. Some investigators, incidentally, allow the possibility of dispersion of liquid by separation from the surface and extraction of its drops by the rapidly exiting gas [233]. Dispersion is particularly characteristic for solid, nonfusible explosives or explosives which become highly viscous liquids when heated.

The significance of dispersion for the performance of chemical reactions within the depth of a charge can be illustrated easily using the example of the combustion of powdered explosives. Under these conditions, the gaseous combustion products (and therefore chemical conversion) can penetrate into the charge and ignite it to considerable depth.

The formation of a suspension of explosive particles here results from the fact that the propagation of the reaction occurs unevenly; into the depth of the

charge through the surface of explosive particles, its rate is greater than the rate of propagation from the surface of particles to their centers. This phenomenon is observed, for example, in the combustion of coarsely dispersed powder with low gravimetric density. In this case, the gaseous combustion products easily penetrate into the gaps between powder particles, combustion occurs through a layer of considerable thickness; the outgoing gases extract the hot powder particles and carry them away.

In the case of utilization of a strongly compressed individual explosive¹⁷, containing no pores, this mechanism of penetration is obviously impossible, unless pores are formed during combustion, i.e. by cracking. However, even a homogeneous reaction in the solid material, occurring with the formation of gases, unavoidably leads in its early stages to disruption of the integrity of the crystalline lattice, to the formation of explosive suspensions in the gaseous decomposition products. If the explosive is kinetically heterogeneous, the conditions of formation of the suspension are even more favorable. When the layer near the flame front is heated, chemical conversion occurs within it. This conversion, in the case of solid explosives, is locally self-accelerating by a topochemical or chain rule, and begins with the appearance of a comparatively few individual reaction seeds. The formation of these centers of decomposition occurs only with considerable difficulty, with activation energy; the growth of the seeds is an autocatalytic or chain process and occurs much more easily, with lower activation energy¹⁸.

An essential role may also be played by the stopped course of the reaction observed in many cases, manifested as the presence of two maxima on the rate curve. During heating, the first local reaction occurs, and continues with the liberation of the acids which carry off a large portion of the material in undecomposed form; after a certain flight time, corresponding to the induction period preceding the development of the second reaction, the particles in this stream ignite, which occurs at a considerable distance from the surface of the condensed phase¹⁹. Indirect evidence in favor of this mechanism is the observation of Belyayev that fulminate of mercury, after being heated for some time at high temperature, burns more slowly. This is how it should be in the light of this hypothesis, since preliminary heating causes partial slow occurrence

¹⁷, ¹⁸, ¹⁹ See p. 186.

of the first reaction, which has an important role to play in the process of dispersion. Garner [234] observed in the thermal decomposition of fulminate of mercury a breakdown of the crystal into a number of fragments during the initial stages of decomposition. During combustion, this breakup should occur more rapidly and might be accompanied by flight of fragments, as was observed by Bouden, et al [235] in the burning of individual crystals of certain explosives.

If we heat calcium azide in a test tube, when ignition occurs the flying hot particles are quite clearly seen: some of them fly quite independently of the general gas stream according to the reactive principle. The source of gases may be more than the chemical reaction alone. If the explosives contain much dissolved air, which is liberated upon heating or volatile products such as water, which is converted in this case into vapor, they will be separated in the form of bubbles as the surface layer entering combustion is heated, and will also aid in the separation of particles of the condensed phase during burning.

With this burning mechanism, the influence of various factors such as pressure, temperature, etc. on combustion may obviously be essentially different than with the normal "heat conductivity" process, since these factors will not only influence the rate of the gas phase in the normal manner, but will also influence the course of the gasifying processes.

Thus, an increase in the pressure, a delay in the outflow of gases will doubtless lead to an increase in the effective temperature in the dispersed layer. In addition to this, the pressure will influence the duration of combustion of dispersed particles, their mean distance of ignition from the point of formation, etc.

Dispersion can have no essential role in the combustion of volatile explosives under ordinary conditions. However, for these also conditions may be created under which dispersion will occur. Let us explain this using the following experiment as an example: we will slowly heat a considerable charge of picric acid; when a certain temperature is reached, rapid decomposition occurs, accompanied by ejection of a group of hot explosive droplets. A similar nature for the process is observed when trotyl, heated to the highest possible temperature, is burned; the burning process pulsates and the acceleration is accompanied by ejection of liquid droplets with the gas.

Table 40
Calculated Combustion Rate of Hexogen, PETN and Tetryl
[according to equation (4.35a)]

A. HEXOGEN

	Pressure, kg/cm ²					Notes
	1	5	10	25	50	
Boiling point, °K	613	667	690	725	760	$c_p = 0.24$ (cal/g·deg) $\eta = 4 \cdot 10^{-4}$ (cal/cm·sec) $E = 41000$ (cal/mol) $\lg A = 15.5$ $p = 1.5$ g/cm ³ $\lambda = 26000$ cal/mol $L = 29.3$ cal/g $T_0 = 293^\circ$ K
$c_p(T_p - T_0) + L$	106.1	119.1	124.6	133.0	141.4	
a_m (calc) g/cm ² ·sec	0.045	0.18	0.30	0.63	1.22	
a_m (exp) g/cm ² ·sec	0.054	0.21	0.33	0.94	1.51	
a_m calc exp	0.83	0.86	0.91	0.97	0.81	

B. PETN

	Pressure, kg/cm ²					Notes
	20	25	40	50	50	
Boiling point, °K	631	640	656	665		$c_p = 0.4$ (cal/g·deg) $\eta = 4 \cdot 10^{-4}$ (cal/cm·sec) $E = 40000$ (cal/mol) $\lg A = 15.8$ $p = 1.5$ g/cm ³ $\lambda = 23000$ cal/mol $L = 17.7$ cal/g $T_0 = 293^\circ$ K
$c_p(T_p - T_0) + L$	152.9	156.5	162.9	166.5		
a_m (calc) g/cm ² ·sec	0.10	0.13	0.18	0.22		
a_m (exp) g/cm ² ·sec	0.38	0.47	0.76	0.97		
a_m calc exp	0.26	0.28	0.24	0.23		

C. TETRYL

	Pressure, kg/cm ²					Notes
	1	12	25	25	50	
Boiling point, °K	583	653	690	687	710	$c_p = 0.23$ (cal/g·deg) $\eta = 2.5 \cdot 10^{-4}$ (cal/cm·sec) $E = 39000$ (cal/mol) $\lg A = 15.4$ $p = 1.5$ g/cm ³ $\lambda = 26000$ cal/mol $L = 19.5$ cal/g $T_0 = 293^\circ$ K
$c_p(T_p - T_0) + L$	86.2	102.3	106.5	110.1	115.4	
a_m (calc) g/cm ² ·sec	0.045	0.25	0.45	0.56	0.81	
a_m (exp) g/cm ² ·sec	0.07	0.36	0.58	0.66	0.89	
a_m calc exp	0.64	0.70	0.78	0.85	0.91	

With extended heating of these explosives decomposition processes start in them, accompanied by the accumulation of autocatalyst. As a result of this, the rate of chemical conversion increases strongly and its probability may become comparable to the probability of evaporation, particularly if we consider the great thickness of the layer in which the reaction can occur in comparison to the surface layer in which evaporation occurs. As a result of this, picric acid heated to 300°C in a large charge does not evaporate noticeably, since centers of intensive decomposition arise; this leads to the flash picture just described. The same thing occurs in the combustion of strongly heated trotyl; evaporation occurs only on the surface layer, while decomposition occurs within a hot layer of considerable thickness and with a high content of autocatalyst. The formation of decomposition centers within the layer leads to their rapid growth as a result of self-heating, and as a result of autocatalysis. Obviously, the number of centers is not great; if there were very many of them, the particles (in this case drops) of explosive would be quite small and the dispersion would be difficult to observe, since the particles would burn quite rapidly.

It is possible that these relationships are fulfilled in the burning of certain solid explosives, for example, nitrocellulose under those ordinary conditions where no visible dispersion is observed. If we change the combustion conditions for the same nitrocellulose in the direction of decreasing rate of formation of seeds and increasing rate of seed growth, we can observe intensive dispersion, as for trotyl.

Thus, combustion with dispersion is a common mechanism of combustion, and the difference in this respect between the secondary and rapidly burning explosives is only that for the latter this mechanism is normal, while for the former it is observed only in certain (unusual) combustion situations.²⁰

There is not sufficient material available to answer the question concerning the reasons for this without limiting ourselves by assuming differences; apparently, this is related to differences in specific surface, as well as rate (activation energy) of appearance of seeds and the rate (activation energy) of their growth under various conditions; for example, very high, or very low rate of appearance of seeds does not favor the appearance of dispersion; a

²⁰ See p. 186.

change in explosive temperature, changing the relationship between the rates of the two processes, should be reflected by the appearance of dispersion.

The conditions of seed growth should also be essential in relation to combustion rate; when unfavorable relationships, the gas formation centers may not develop.

In any case, the general theory of combustion should analyze not only the case of combustion of liquid explosives at low temperatures under conditions of even evaporation analyzed by Zel'dovich and Belyayev, but also the case when a significant portion, sometimes most of the undecomposed explosive is carried away by the stream of gaseous combustion products and continues to decompose and react with them rather far from the boundary of undecomposed explosive, and sometimes avoids chemical conversion entirely.

One aspect of this process--the conversion of the condensed phase to a suspension of explosive particles in the gaseous conversion products--can be described on the basis of the theory of the leading exothermic reaction in the condensed phase outlined above, in which case the maximum temperature of the condensed phase is limited by a certain limit. As applicable to boiling explosives, this limit is taken as the boiling point; as applicable to dispersed explosives, a certain analog of this temperature can be used, when the rate of the dispersing reaction becomes so great that the condensed phase goes over from its initial state to the state of a suspension.

The applicability of this theory to cases of dispersion is apparently the reason for the similarity of the dependences observed in the combustion of dispersed and volatile explosives at high pressure or dispersed and slightly volatile explosives where the reaction in the condensed phase occurs at low pressures.

One of the results of dispersion which distinguishes combustion in this regime from the case when the leading exothermic reaction in the condensed phase does not form suspensions, but rather only gases, is the presence of a large contact surface between the gaseous reaction products and the particles in the suspension. Therefore, heat exchange increases strongly, and the quantity of reacting material per unit area of charge cross-section increases also. This is reminiscent of the process which occurs as hot gaseous combustion products penetrate into the depth of a powdered, porous charge. The difference is that in one case the gases penetrate into the powder, while in the other case the

powder (formed by dispersion of particles) penetrates into the gas.

Up to this point, we have discussed the dispersing reaction, occurring with liberation of heat and therefore leading the process of combustion.

This dispersion will be called "active". We can imagine another case--that of "passive" dispersion, when this dispersion is not leading, but is forced, i.e. occurs under the influence of heat influx from the layer of suspension reaction in the gaseous products adjacent to the surface of the condensed explosive.

If the temperature of the suspension is sufficiently high, the rate of heat transfer would be great; the rate of mixing of the dispersion zone will also be high. Incidentally, the capability for burning may not be too great here; with too intensive dispersion, the gas portion of the suspension may not be able to "cook" the many particles arriving in it so that the particles, cooling the hot zone, may lead to attenuation of combustion. The corresponding minimum rate of combustion may be relative great (as compared to volatile explosives) since everything depends on the rate of "cooking" and the rate of arrival of the "food" which should not be too great.

In just the same way, the influence of various factors such as pressure on the combustion rate will be dual, consisting of the influence on the rate of heat liberation in the hot zone and the rate of dispersion. In principle, it is possible that an increase in pressure, i.e., increases the rate in the hot zone but a strong decrease in dispersion leads to a decrease in the combustion rate.

The problem of which materials and conditions produce "active" or "passive" dispersion may be directly explained only by establishment of the temperature profile and heat liberation profile during the course of combustion. Indirect conclusions in this respect can be made by certain data produced from investigation of thermal decomposition and combustion of a number of rapidly burning explosives.

Footnotes

1. To p. 137. The hypothesis of Michelson and Mallard-LeChatelier was developed for gases, but is applicable without essential changes to the combustion of condensed explosive systems.
2. To p. 143. In comparing these probabilities, incidentally, it is necessary to consider that only those molecules on the surface of the liquid can evaporate, while the molecules in the adjacent layers heated to rather high temperatures can also react.
3. To p. 154. In order to reduce a value of velocity corresponding to the experimental value in this calculation, the reaction temperature must be assumed $\sim 870^{\circ}\text{C}$. Since with stable combustion the rate of propagation of all zones should be identical, it is possible that it is at this temperature that the first stage of the process occurs, which is not the leading stage under these conditions.
4. To p. 159. Recently, Belyayev analyzed one more possible reason for this divergence. He assumed that the leading reaction in the gas phase, even at relatively low pressures, does not occur at the maximum temperature (calculated from the composition of the combustion products), but at a lower "effective" temperature, which can be determined in principle by measuring the temperature profile of the combustion wave using thermocouples [270] (editors note).
5. To p. 160. For certain explosives at high pressures in the area of high temperatures, not far from the autoignition temperature, a sharp increase in temperature factor is observed, but this increase has a different reason, being related to exothermal decomposition in the condensed phase and, possibly, to excitation of the melted layer.
6. To p. 162. From this we must conclude that in order to reduce nitric oxide, much greater increases in combustion temperature are required than that achieved by increasing the initial temperature of the explosive by 100°C .
7. To p. 164. The only exception is the case (possible in principle) when the rate constant of the secondary exothermic reaction is very high in comparison with the rate of the primary reaction, and the products of the latter react immediately with each other so that the reaction distribution by zones analyzed below is not observed. In this case, the rate of

15. To p. 172. When solid, meltable explosives are burned, equation (4.35) can be written in the form:

$$u_{\infty} \approx \left[\frac{2\gamma p_0 e^{-E/RT_0}}{c_p(T_0 - T_0) + L} \cdot \frac{RT_0^2}{E} \right]^{1/2} \text{ g/cm}^2 \text{ sec}, \quad (4.35a)$$

where L is the latent heat of melting of the explosive (in cal/g); ρ is the density of the liquid phase (in g/cm³). (Editor's note).

16. To p. 175. A relationship between volatility and rate of thermal decomposition is assumed.

17. To p. 178. In the case of mixtures whose exothermic conversion is possible as a result of the interaction of components of the phases, uneven propagation of combustion can obviously occur in the form of "contact" combustion (see p. 231 [of original text, not requested for translation]) when there are no pores. For strongly compressed individual explosives, there is no reason to assume preferential propagation of the chemical reaction along the particle surface in comparison with propagation into the depth of the particle.

18. To p. 178. The nonhomogeneous beginning and course of the chemical process facilitates kinetic heterogeneity of the material in the case of solid powder. The activation energy on the surface and within the particle may be quite different. In the case of rapid processes, self-heating due to the exothermic reaction may also be very important.

19. To p. 178. This process of combustion can be imaged more clearly if we assume that we are dealing with a powdered mixture of the particles of two explosives—with low and with high flame temperatures. The case is possible when one material will burn, while the particles of the other will be carried away by the gas stream, while at low combustion rates with strong cooling of the gases they may even fly out of the tube unburned.

20. To p. 181. There is reason to believe that this mechanism appears during detonation as well. When an explosive is compressed by a shock wave (even in the case of a homogeneous material) decomposition may arise at individual points and develop in the form of centers using the thermal or even the chain mechanism, which leads to dispersion of the explosive. This method of formation of the mixture of explosive particles and decomposition products in the front of the detonation wave, which is permitted by modern detonation theories, seems most probable to us for homogeneous explosives.

conversion is limited by kinetic characteristics of the primary reaction, while the temperature is limited by the thermal effect of the exothermic reaction.

8. To p. 165. The thermal conductivity of the gas does not depend on the pressure, the quantity of energy per unit volume of gas being proportional to pressure, while burning time is less.

9. To p. 166. In calculations, several variants are possible: we can assume the order of the reaction to be 1 or 2, the factor before the exponent equal to the number of collisions or less, the thermal effect can be calculated from the experimentally established gas composition or this composition can be adjusted by certain assumptions. With several of these variants the activation energy calculated by the combustion rate is similar to the activation energy of slow thermal decomposition.

10. To p. 166. This quantity is determined primarily by the value of $e^{-E/2RT_0}$. If E is assumed to be 40,000 cal at $T = 1800^\circ$, as the temperature is increased by 100° the value of $e^{-E/2RT_0}$ increases by only 1.35 times; if with the temperature unchanged the activation energy is not 40,000, but 50,000 cal, then $e^{-E/2RT_0}$ is decreased by only four times.

11. To p. 168. The pressure at which the secondary flame appears is decreased as the diameter of the tube in which combustion occurs is increased.

12. To p. 168. If the activation energy of the leading reaction is not too low; judging from the high temperature dependence $u(T)$, this condition is fulfilled.

13. To p. 169. A slight contradiction to this explanation, based on the autonomous nature of term A, is the fact that as the initial temperature is increased, it increases by the same number of times as B, as was established for nitroglycerin powder H.

14. To p. 171. True, it must be considered that as the pressure is increased the heat of evaporation is decreased, which favors evaporation in its competition with chemical conversion; also, at increased pressures the burning rate is higher, i.e. the time which the heated layer spends at high temperature is less, and consequently the possibility of development of chemical self-acceleration within the layer is also less.

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(U) This book essentially presents a review and summary of experimental and theoretical findings obtained in the field of combustion processes in explosives. The author, who died before completing his review of the book for publication, was one of the foremost Soviet specialists in the field, and many of the findings and basic principles cited in the book are either his or those of his school. This is particularly true with respect to the material on the theory of combustion and thermal disintegration of secondary explosives, and the analysis of critical phenomena and to the physical essence of the difference between the properties of a number of explosives. Briefly summarized, the book is concerned with the principal forms of explosives and their capacity for chemical conversion (i.e., stable combustion, nonsteady state combustion, and detonation), the main problems of chemical kinetics in the initiation and development of an explosion as a function of changes in temperature, and the slow combustion of (principally) condensed substances. The book is intended for students, engineers and scientific workers specializing in physical chemistry and chemistry. The following persons were mainly responsible for preparing the original manuscript for publication: B. S. Svetlov, A. P. Glaskova, B. N. Kondrikov, A. I. Gol'binde (deceased).

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